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TREATMENT OF PESTICIDE-LADEN WASTEWATERS FROM
ARMY PEST CONTROL FACILITIES BY ACTIVATED CARBON
FILTRATION USING THE CARBOLATOR TREATMENT SYSTEM

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Water	

20. ABSTRACT *(Continue on reverse side If necessary and identify by block number)*

A treatment system based on the recirculation of pesticide-contaminated wastewater through a bed of granular activated carbon was found to be of particular use to the small waste generator. In pilot-scale tests, a CARBOLATOR 35B^R was filled with 45 lb of granular activated carbon and challenged with 400 gallons of water containing a mixture of seven different pesticides at concentrations of 20, 60, and 100 mg/L of each pesticide. The

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20. Abstract (continued)

decline in pesticide concentration was exponential with pesticides showing
varying affinity for the carbon. Following successful pilot runs, two
successful field tests were made with the system using pesticide-laden
wastewater from a pest control facilty at Fort Eustis, VA.

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BACKGROUND

Recognizing the health and environmental problems associated with pest control operations, the US Army Training and Doctrine Command (TRADOC) designed and built a pest control facility at Fort Eustis, VA, that meets all current health and environmental regulations for such a facility. A specially designed drainage system collects all wastewater containing pesticides produced as a result of mixing operations, clean-up of pesticide dispersal equipment, and rinsing of empty pesticide containers. As designed, wastewater would be retained in storage until a sufficient volume was collected for commercial disposal. Public Law 89-272 (Resource Conservation and Recovery Act) places ultimate responsibility for disposal of hazardous wastes on the generator. Since the Army's responsibility for these wastes does not end once they are removed from the installation, it would be advantageous to have a local treatment system at the pest control facility.

Prior to construction of the Fort Eustis pest control facility, TRADOC requested assistance from the US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) in investigating the feasibility of using an activated carbon filtration/adsorption column system to treat the pesticide-laden wastewater. If these methods were found feasible, USAMBRDL would evaluate a carbon system to treat the wastewaters and provide design criteria data for TRADOC to use in Army pest control facilities.

During the period July 1978 to August 1979, a packed bed carbon column filtration system was built and tested at USAMBRDL, Fort Detrick, MD. This system (Figure 1) consisted of six 5.25-inch ID columns (in series) filled with 4 ft of activated carbon resting on a gravel support medium, a traditional packed bed pressurized filter. Upon completion of the pest control facility, this filtration system was transferred to Fort Eustis, VA. Field tests of this filtration system were carried out during FY80 and FY81.

Concurrent with the FY81 field testing of the packed bed carbon filtration system, a commercial carbon filtration system (CARBOLATOR^R)* was also tested. The CARBOLATOR was believed to have greater potential than the packed-bed system for solving the waste treatment problem at pest control facilities.

The CARBOLATOR 35B water purification unit (Figure 2), manufactured by the SETHCO Corp., NY, was tested at the USAMBRDL Unit Process Laboratory at Fort Detrick, MD. In these tests, the CARBOLATOR was challenged with 400 gallons of water containing seven different pesticides at concentrations from 20 mg/L (per pesticide) to 100 mg/L (per pesticide). These tests were successful in removing all pesticides from the water. Field tests of the CARBOLATOR were conducted in-place at Fort Eustis, VA, during June and September of 1981.

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* CARBOLATOR 35B is a registered trademark of the SETHCO Manufacturing Corporation, Freeport, New York. Use of trademarked name does not imply endorsement by the US Army, but is used only to assist in identification of a specific product.
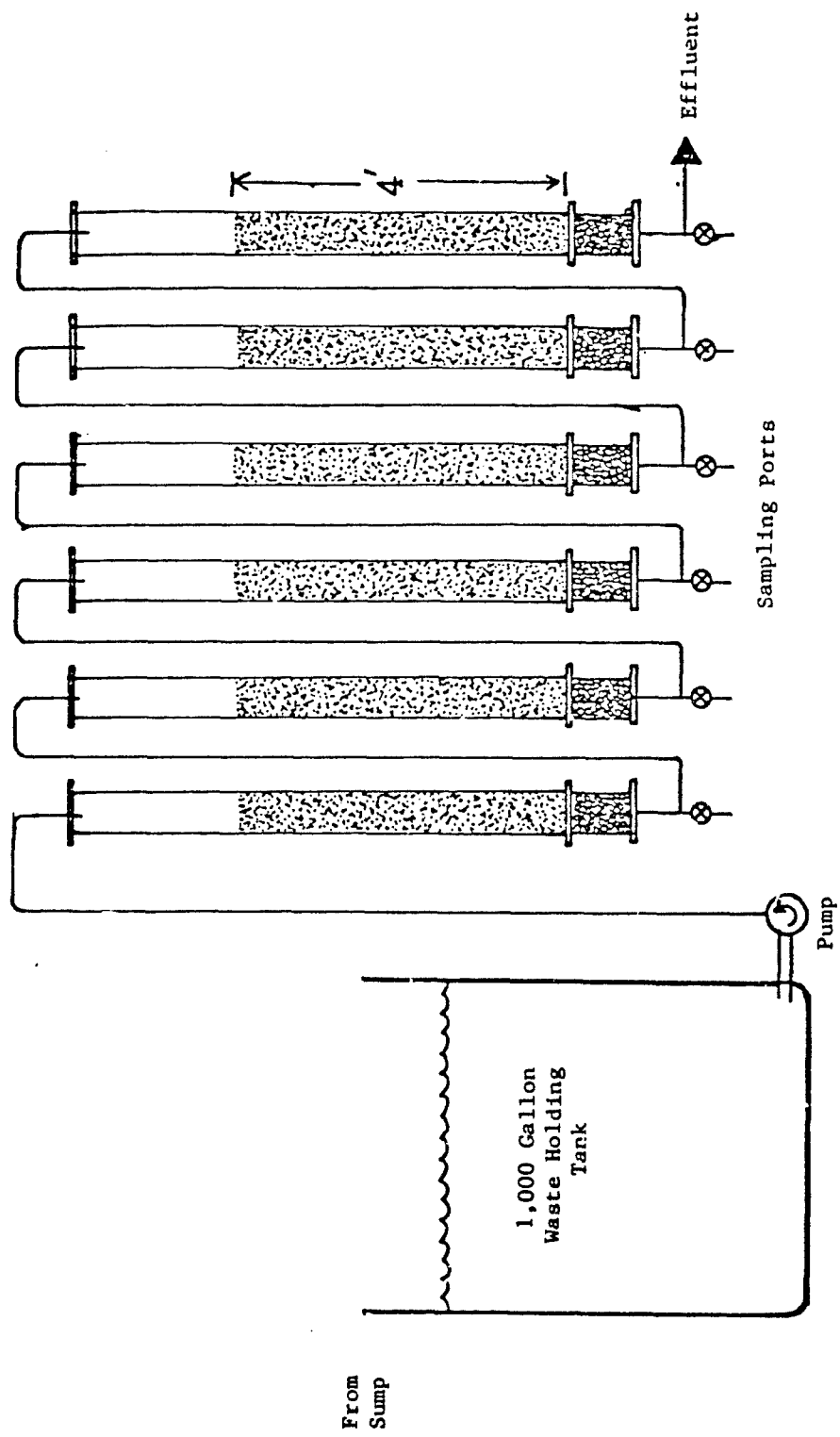
Figure 1. The flow-through carbon filtration system installed at Fort Eustis in Spring of 1980.

CARBOLATOR® 35

AUTOMATIC FIVE-WAY PURIFICATION IN ONE COMPACT UNIT

...for tanks to 3000 gallons

with MAGNETIC PUMP

with IN-TANK PUMP
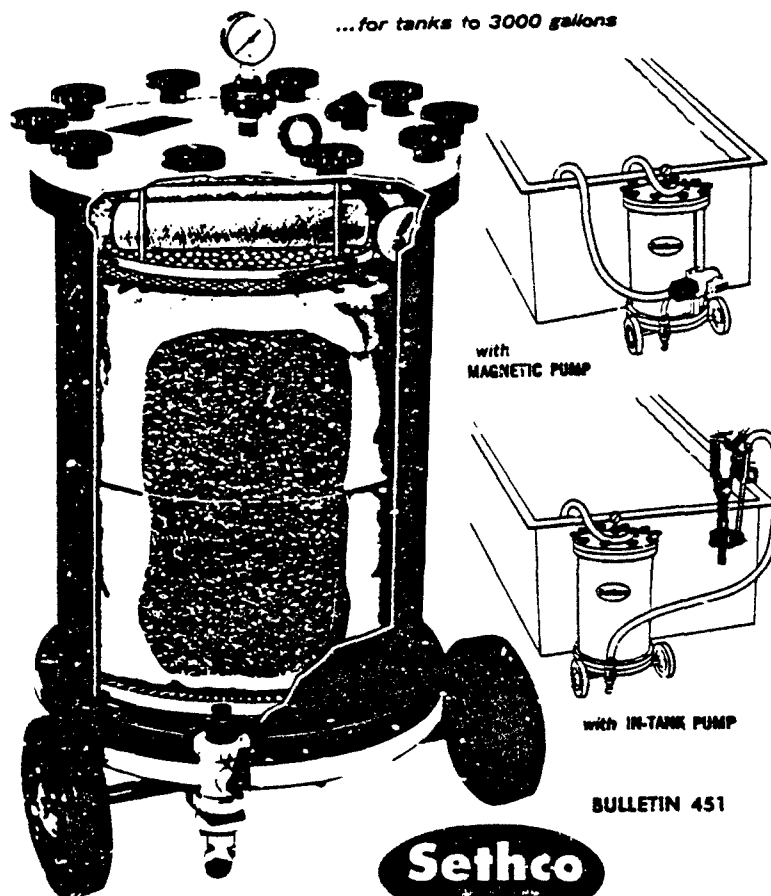
BULLETIN 451

Sethco

One Bennington Ave., Freeport, New York, U.S.A. 11520
516 MAyfair 3-4220

GL-89

Figure 2.   CARBOLATOR 35B.

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OBJECTIVE

It is the objective of this report to present the results obtained from testing a carbon filtration system based on the commercial CARBOLATOR. The system was used for the removal of pesticides from contaminated wastewater. Both laboratory tests and on-site trials of this system are presented and discussed.

METHODS AND MATERIALS

DESCRIPTION AND OPERATION OF THE CARBOLATOR 35B CARBON FILTRATION SYSTEM

The CARBOLATOR, a commercial unit, operates by the recirculation of a volume of wastewater through a bed of carbon (Figures 2 and 3). This system has several advantages when compared to a flow-through system of carbon columns. One of the advantages is found in its design. The CARBOLATOR is lightweight and portable, consisting of an 18-gallon reinforced epoxy tank with an O-ring seal cover. Two porous polypropylene bags, which hold the granular carbon, are placed in the tank and the top is sealed. Pesticide-contaminated water is pumped continuously into the bottom of the CARBOLATOR and upward through the carbon bed. The water is returned to the waste holding tank. The fluidized system tends to eliminate channeling and improves the contact between the carbon and contaminated wastewater. Moreover, the bed does not compact and induce a large pressure drop. In contrast, a pressurized packed bed filter, Figure 1, tends to induce large pressure drops and channeling through bed compaction. Furthermore, the packed bed system requires continual monitoring for breakthrough to ensure a pesticide-free effluent. The CARBOLATOR continually recirculates water back to the holding tank, eliminating the need for continuous monitoring. After a specified time, the tank can be sampled for residual pesticides.

Operation of the CARBOLATOR system can be mathematically described by using a differential mass balance. With regard to the flow diagram of Figure 3, the following nomenclature will be used:

Q = Flow rate through the carbon bed. This value is constant.

V = Volume of solution in the holding tank. This value is also constant.

x = Amount of pesticides in the solution at any given time (absolute weight).

k = Pesticide fraction removed across the carbon bed (removal "efficiency").

1-k = Pesticide fraction remaining in the recirculation stream.

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$$\frac{C_t}{C_o} = e^{-\left(\frac{q\,t}{V}\right)}$$
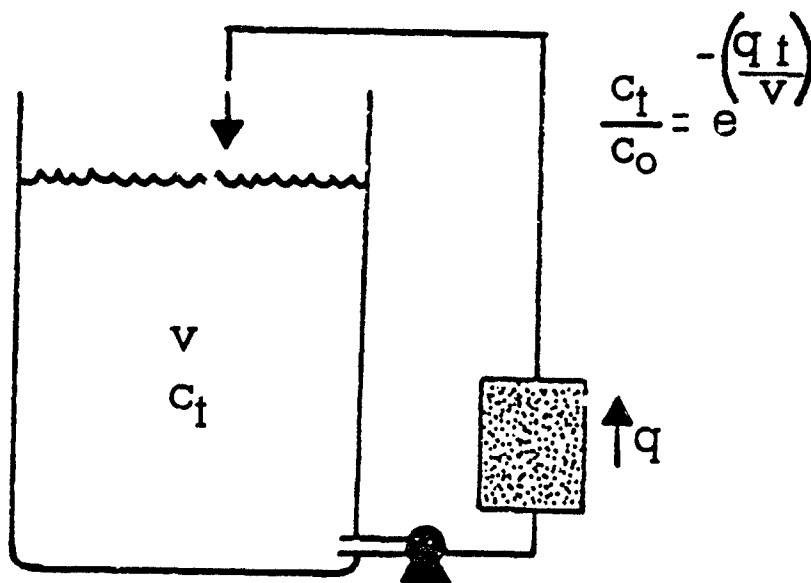
Figure 3. The CARBOLATOR system.

Assumption = The contents of the tank are at all times completely mixed.

$\frac{dx}{dt}$ = rate of pesticide removal

in = Weight of pesticide recirculated back to the holding tank in a given time increment, dt.

out = Weight of pesticide leaving the holding tank to go to the CARBOLATOR in the same time increment, dt.

Therefore,

$$\frac{dx}{dt} = \text{in} - \text{out} \tag{1}$$

The rate at which pesticides leave the tank ("out") can be described as $\frac{Qx}{V}$, where $\frac{x}{V}$ is in effect the pesticide concentration at any given time. The rate at which pesticides are recirculated back to the tank ("in") can be described as $\frac{Qx}{V}$ (1-k), where $\frac{x}{V}$ (1-k) is the pesticide concentration in the stream leaving the CARBOLATOR based on the removal efficiency of the CARBOLATOR. (If the efficiency was 100 percent, this expression would be zero.) Insertion into Equation 1 gives

$$\frac{dx}{dt} = \frac{Qx}{V} (1-k) \; \frac{-Qx}{V} \tag{2}$$

After simplification, Equation 2 becomes:

$$\frac{dx}{dt} = \frac{-kQx}{V} \tag{3}$$

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Equation 3 can be integrated to give:

$$\ln \frac{X_1}{X_o} = \frac{-kQt}{V} \tag{4}$$

where X_1 is the weight of pesticide left at time t and X_o is the initial weight of pesticide.

By redefining X, Equation 4 can be further simplified. Because X is the weight of pesticides in the solution at any given time, the term CV can be freely substituted. Because V is constant, Equation 4 can be rewritten

$$\ln \frac{C_1}{C_o} = \frac{-kQt}{V} \tag{5}$$

or more traditionally:

$$\frac{C_1}{C_o} = e^{-kQt/V} \tag{6}$$

By converting Equation 5 from natural ln to log the equation becomes:

$$\log \frac{C_1}{C_o} = \frac{-kQt}{2.303 \ V} \tag{7}$$

Equation 7 readily lends itself to graphical interpretation on semi-log paper. A straight line results with a slope of $\frac{-kQ}{2.303V}$. Since both Q and V are constant, the slope is strictly a function of removal efficiency. If k is assigned a value of 1, Equation 7 gives the theoretically shortest time for complete treatment to a given limit (C_1/C_o). Equation 7 allows for plotting concentration versus time. All of the plots shown in Appendixes A, B, and C are based on this form.

EVALUATION OF ACTIVATED CARBONS FOR DIAZINON ADSORPTION

Diazinon adsorption isotherms were obtained for the activated carbons listed in Table 1. The isotherm data were evaluated to determine if there were significant differences in the carbons tested. From this data, it was determined that F-300 by Calgon Environmental Systems was the most effective in removing diazinon from water.

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TABLE 1. ACTIVATED CARBONS EVALUATED IN ISOTHERM STUDIES WITH DIAZINON

Source	Carbon Identification
Westvaco Chemical Sales Division Covington, VA 24426	Nuchar WV-G, 12 x 10 mesh[a] Nuchar S-A Nuchar WVW, 8 x 30 mesh[a] Nuchar Aqua
ICI America, Inc. Wilmington, DE 19899	DARCO HD 3000, 325 mesh, DXL-0-6431
Barnebey Cheney Columbus, OH 43219	PC 1333[a] NW 8728
North American Carbon, Inc. Box 19737 Columbus, OH 43219	P 100, lot 2022, 21 Dec 77
Calgon Environmental Systems P.O. Box 6768 Bridgewater, NJ 08807	Filtrasorb, F-300, pulverized, PXX
Witco Chemical Corp. 277 Park Ave. New York, NY 10017	Witcarb[TM], Grade 950, 12 x 30 mesh[a]

a. Granular carbons were ground to 325 mesh for isotherm studies.

The procedure for determining the carbon adsorption isotherms was as follows:

1. Samples of 10, 15, 25, 35, 50, 65, 80, 95, 110, 135, and 165 milligrams of dry powdered carbon were weighed and transferred to 50-mL capacity amber glass bottles.

2. To each bottle with carbon, 3 mL of 0.5 M pH 7.0 phosphate buffer was added, followed by 30 mL of a suspension of the diazinon emulsifiable concentrate in water. The final concentration of diazinon was 1,500 mg/L.

3. The bottles were sealed with a Teflon[R]-lined cap and agitated vigorously for 2 hours on an automatic shaker.

4. The contents of each bottle were allowed to stand 1 hour, then filtered by suction through two discs of 4.25-cm diameter #50 Whatman filter paper set into a Buchner funnel. The filtrate was refiltered if there was any carbon observed in it.

5. The concentration of pesticide in each filtrate was determined by gas chromatography after extraction from the aqueous phase with an appropriate organic solvent.

6. The concentration of pesticide found in each filtrate (Y-axis) was plotted against the weight of carbon used for that sample (X-axis).

Figure 4 shows the adsorption isotherm for powdered Calgon F 300, which was the carbon chosen for large-scale column and CARBOLATOR testing.
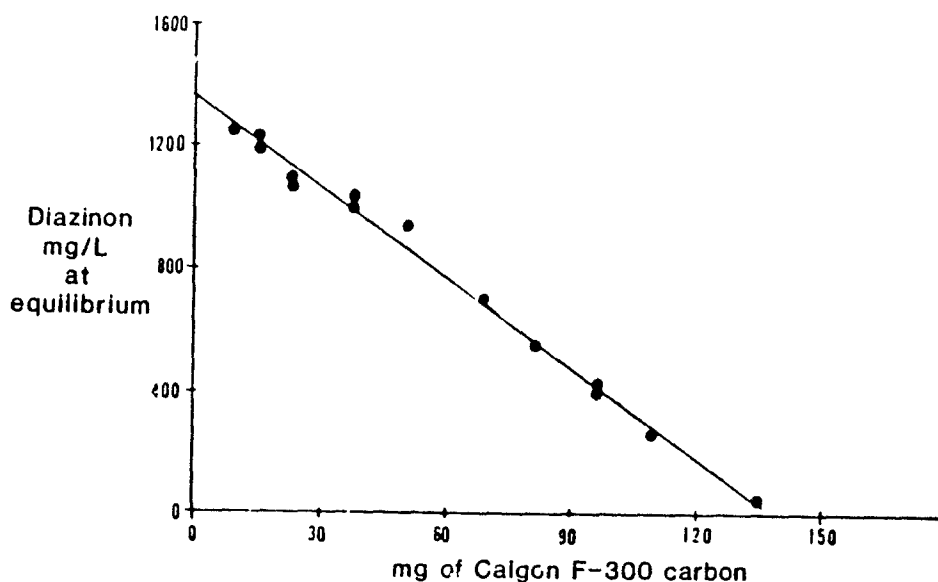
Figure 4.   Adsorption isotherm of Calgon F-300 powdered carbon.
            Volume of solution containing diazinon was 33 mL.

SYNTHETIC PESTICIDE-LADEN WASTEWATER

Between 1977 and 1981 samples of wastewaters generated at the pest control facilities at Fort Eustis, VA, and Fort Knox, KY, were obtained and analyzed to determine the composition of typical wastes. Additionally, conversations with pest control supervisors were held to determine the types and quantities of pesticides employed at these sites. Table 2 shows the composition of such waters at these sites over this time period. From this information, the types of pesticides that would be used in the laboratory phase of testing the CARBOLATOR system were determined. The names and structures of the pesticides chosen for a synthetic waste are shown in Table 3.

TABLE 2.   COMPOSITION OF WASTEWATERS FROM PEST CONTROL OPERATIONS
AT TWO SITES BETWEEN 1977 AND 1981

| | Pesticide Concentration, mg/L | | | | | | | |
| | Fort Eustis, VA | | | | Fort Knox, KY | | | |
Pesticide	Oct 77	Mar 81	Aug 81	Oct 81	Oct 77	May 79	Oct 80	Sep 81
Chlordane	11	<0.1	<0.1	<0.1	20	126	<0.5	0.1
Dursban	200	5	<0.1	19	51	35	750	12
Diazinon	409	6	1	10	90	107	410	416
Dimethoate	--[a]	<0.1	48	17	--	--	<2	56
Ronnel	--	<0.1	<0.1	<0.1	--	--	<2	--
Malathion	18	201	33	82	16	6	44	6
Baygon	83	72	3	41	15	82	64	0.1
2,4-D ester	--	--	--	--	--	--	--	--

a. Not analyzed.

GAS CHROMATOGRAPHIC ANALYSIS OF WATER FOR PESTICIDES

Analyses of water for pesticides were performed by gas chromatography (GC)
using a flame ionization detector.   Solvents used for extraction were checked
for purity or interferences by GC.   Standards were prepared by mixing various
pesticide formulations with water.   These aqueous standards were extracted in
the same manner as unknown solutions.   The standard concentrations encompassed
the concentration range of unknowns to be identified.   A standard curve con-
sisted of a set of four concentrations.   The conditions for GC analysis was
guided by the pesticide composition expected in the water.   Mixtures, such as
those employed in the synthetic waste and those encountered in the field were
analyzed on a 6 ft, 3 percent OV-1 on GAS CHROM Q column.   A typical chro-
matogram of such a mixture is shown in Figure 5.
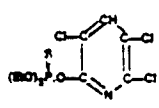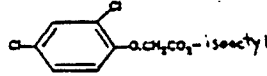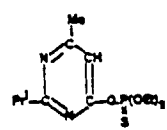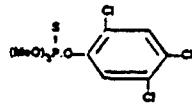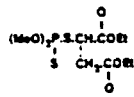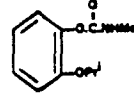
Figure 6 shows a flow chart outlining the protocol used for analysis of
both synthetic wastewater and waters encountered in field tests at Fort
Eustis, VA.

ON-SITE ANALYSIS OF WASTEWATERS BY THIN-LAYER CHROMATOGRAPHY

An effort was made to develop a field method to identify qualitatively and
semi-quantitatively the pesticide constituents of a pesticide-laden waste-
water.   Such a field method was developed through thin-layer chromatography
(TLC).   Thin-layer chromatography gives a presumptive test for the presence of
specific pesticides and an estimate of their concentrations within
30 minutes.   It may also reveal the presence of unknown substances.   The field
application of TLC requires a trained operator using inexpensive equipment.
The following protocol describes the on-site use of TLC:

Extract a 200-mL aliquot of the wastewater with 25 mL of CH_2Cl_2 twice in a
250-mL separatory funnel.   Combine the CH_2Cl_2 extracts and add to this mixture
a few grams of anhydrous Na_2SO_4 to adsorb moisture.   Pour a portion of the

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TABLE 3. NAMES AND STRUCTURES OF PESTICIDES USED TO
PREPARE A SYNTHETIC WASTEWATER

COMMON NAME	ALTERNATE NAME	CHEMICAL NAME	STRUCTURE	SOLUBILITY IN WATER
Chlorpyrifos	Dursban	O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate		2 ppm (35°)
2,4-D-LVE	---------	Isooctyl ester of 2,4-dichlorophenoxy-acetic acid		practically insoluble
Diazinon	---------	O,O-Diethyl-O-(2-isopropyl-6-methyl 4-pyrimidinyl) phosphorothiate		40 ppm (25°)
Dimethoate	Cygon	O,O-dimethyl-S-(N-methylcarbamoylmethyl) phosphorodithioate	(MeO)₂PS.S.CH₂CO.NHMe	25,000 ppm (room temp.)
Fenchlorphos	Ronnel	2,4,5-Trichlorophenyl phosphorothionate		40 ppm
Malathion	------	Diethylmercapto-succinate S-ester of O,O-dimethylphosphoro-dithionate		145 ppm (25°)
Propoxur	Baygon	2-Isopropoxy-phenyl N-methyl carbamate		2000 ppm (20°)

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Figure 5. Gas chromatogram showing separation of seven pesticides. Conditions: 6′, 3% OV-1 on GAS CHROM Q, 100-200 mesh, $160^o \xrightarrow[16^o/min]{} 240^oC.$

Figure 6. Flow chart showing the qualitative and quantitative analysis of Fort Eustis wastewater.

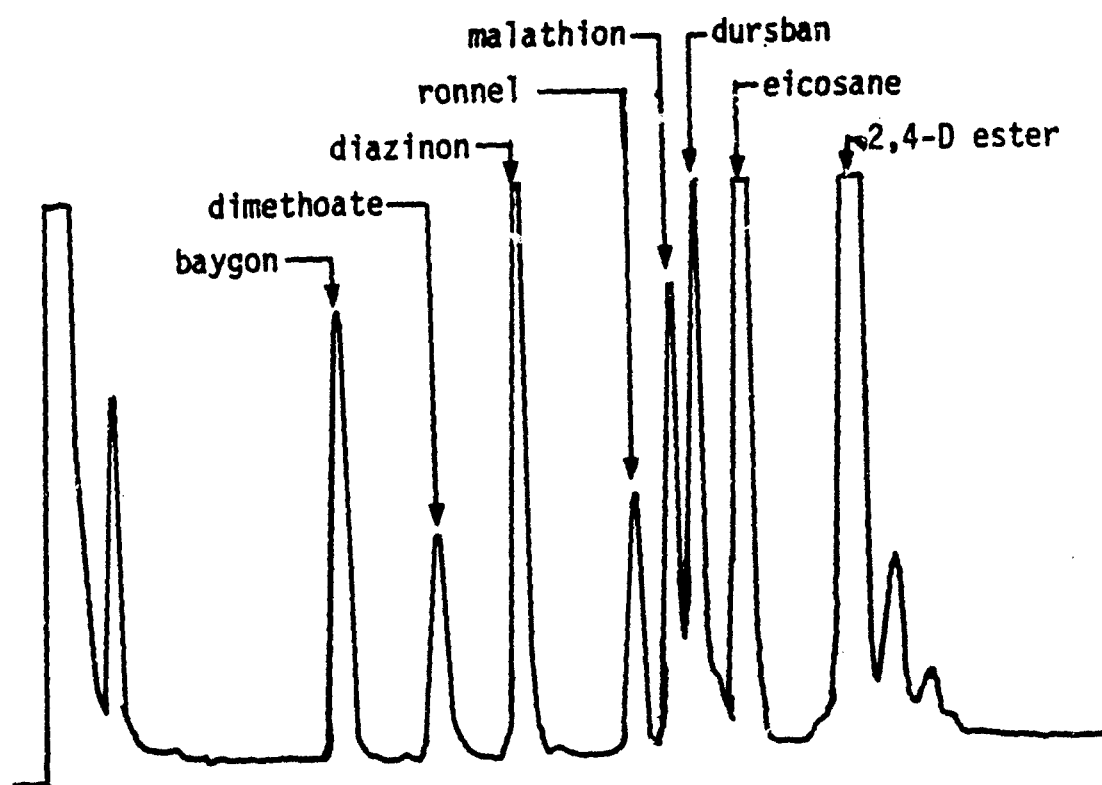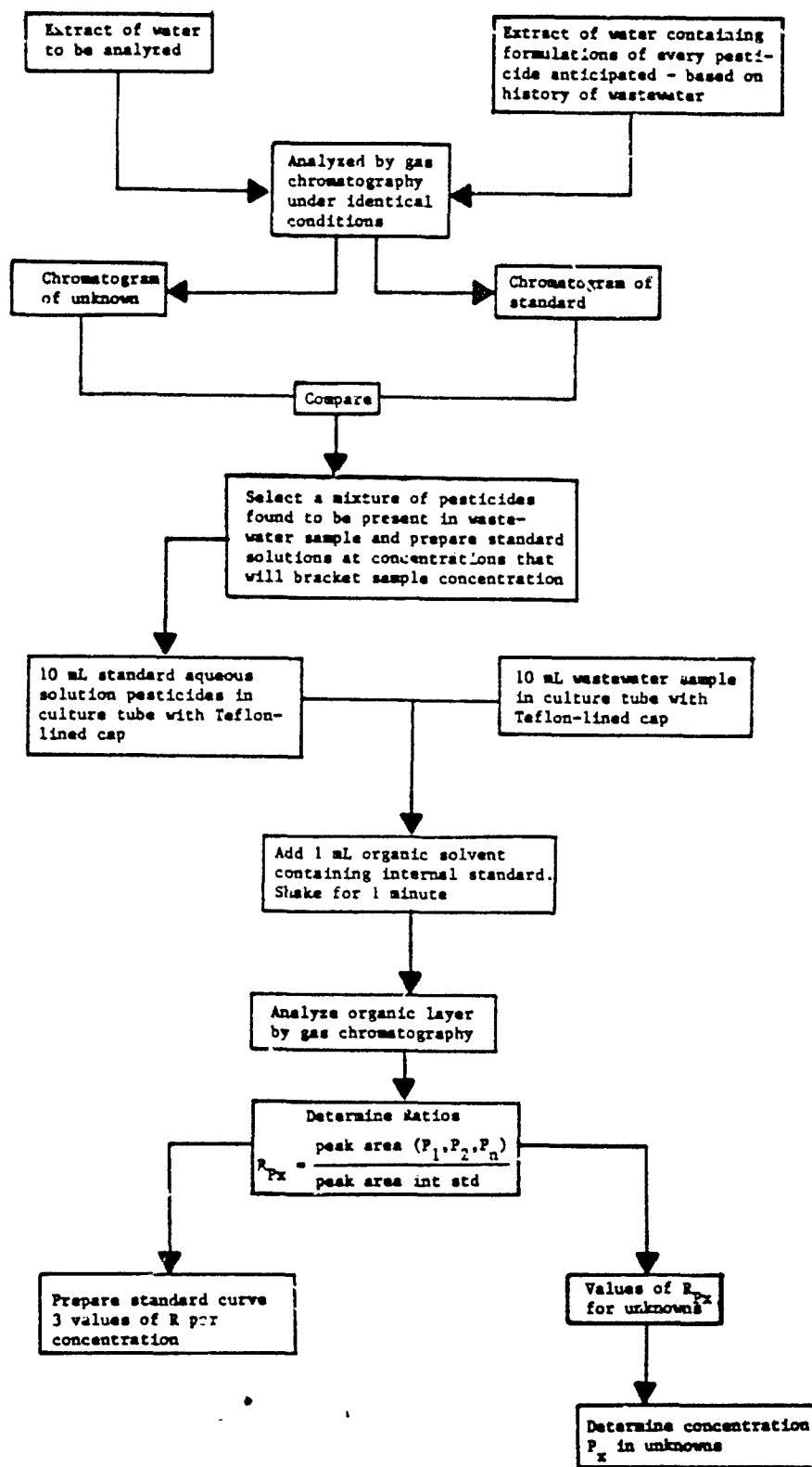CH$_2$Cl$_2$ extract into a 20-mL scintillation vial and allow the CH$_2$Cl$_2$ to evaporate in the open air. As the CH$_2$Cl$_2$ evaporates, add more of the extract until the entire CH$_2$Cl$_2$ extract has been reduced to an oily residue. This residue will contain the pesticides that were suspended or dissolved in the wastewater. A heat gun (hair dryer) may be used to hasten evaporation of the CH$_2$Cl$_2$, but care must be used to prevent loss of the extract by too vigorous boiling. Prior to analysis by TLC, reconstitute the residue in the vial with 1 mL of fresh CH$_2$Cl$_2$. Place 10 µL of this solution in a small spot, 1 cm above the bottom of a TLC plate (E. Merck, Silica gel 60, GP-254). At 1 to 2 cm to either side of this spot, place 10 µL of a solution containing several pesticides of known concentration. Then place the TLC plate into a developing jar containing a suitable solvent. When the solvent has risen about 12 cm by capillary movement, remove the TLC plate from the jar, air dry, and observe under UV light. Although the silica gel contains a fluorescent substance, any UV-absorbing substances will show up as dark spots. Outline any observed dark spots in pencil. Finally, spray the TLC plate with an acetone solution of TCQ (N,2,6-trichloro-p-benzoquinoneimine) and heat with the heat gun until colored spots appear. Spraying with TCQ and the heating of the TLC plate should be done in the open air to minimize the irritancy of this reagent.

The TLC spots found in the wastewater extract are matched with those of the known pesticide mixture. This gives qualitative information regarding the wastewater extract. The relative sizes of matching spots gives a semi-quantitative estimate of the concentration of pesticide in the extract. A TLC plate where six pesticides have been separated and made visible by this procedure is shown in Figure 7.

EXPERIMENTAL PROCEDURE FOR LABORATORY-SCALE SIMULATION OF THE CARBOLATOR

It was desirable to evaluate the effectiveness of the CARBOLATOR concept on a solution containing one or more pesticides without resorting to the full-scale (400 gallons of wastewater) treatment system. In order to simulate the recirculation of a pesticide-laden wastewater through a bed of carbon, the bench-scale apparatus shown in Figure 6 was assembled. By treating water containing several pesticides simultaneously in this apparatus, it was possible to determine their relative rates of adsorption by carbon. It was also possible to evaluate various types of granular carbon with this apparatus. The following procedure was used:

Measured amounts of various pesticide formulations are poured into the 5-liter Erlenmeyer flask containing 4 liters of tapwater at room temperature. While this mixture is being stirred, 100 grams (dry weight) of wet carbon is placed into the glass column. This carbon is soaked in water 24 hours prior to use. Clean water (about 500 mL) is passed through the carbon bed (backwashing) to remove carbon fines. The water is then drained from the carbon column, and a connection is made between the stirred reservoir and the bottom of the carbon column through a peristaltic pump. The neoprene stopper is placed at the top of the glass column, and the rubber hose attached to a glass tube in this stopper is led into the flask. The pump is turned on and adjusted to the desired flow. When the water has passed the top of the carbon bed, the carbon column is tapped to dislodge air pockets. When the water begins to spill back into the reservoir, a timer is started (t_o). Prior to starting of the pump, an aliquot (3 mL) of the test water is removed. This
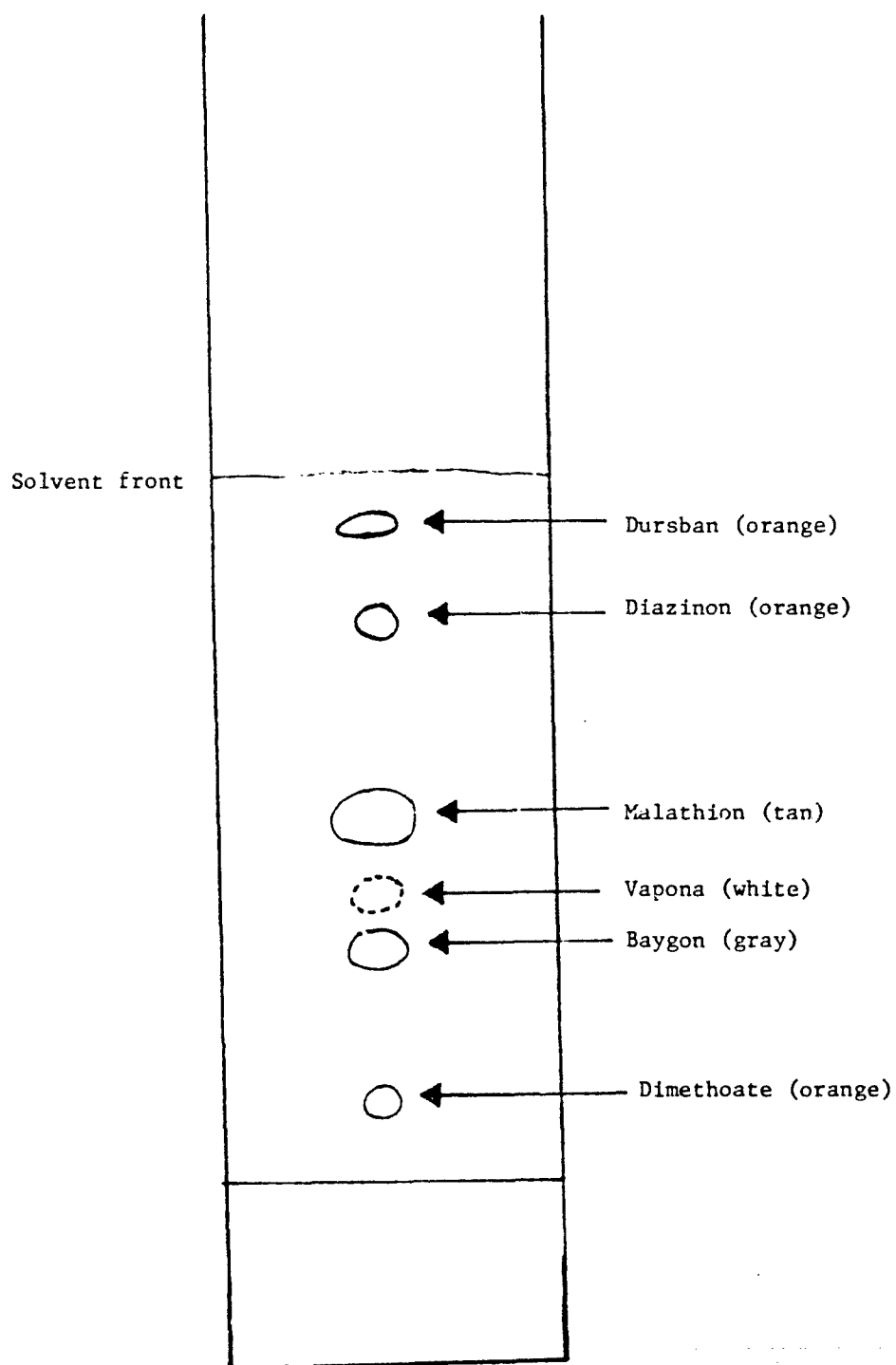
Figure 7. Thin-layer chromatogram of a mixture of six pesti-
cides. Ten microliters of 1,000 ppm solution on
silica gel. Developed by hexane/acetone = 8/3 (V/V).
Visualized by spray of TCQ (N,2,6-trichloro-p-
benzoquinoneimine; 0.5 g in 100-mL acetone) followed
by heating at 100°C until spots appear.

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is used to prepare a standard curve from which will be derived the concentration of pesticides in the samples. At various times during this recirculation, 1-mL, 5-mL, or 10-mL aliquots are removed from the reservoir and placed into screw-cap (teflon-lined caps) tubes containing 1 mL of methylene chloride (CH_2Cl_2) which has been spiked with 20 ppm of eicosane (internal standard). The aqueous sample is extracted with the 1 mL of CH_2Cl_2. This extract is analyzed by gas chromatography (FID).

Figure 8.   Apparatus designed to simulate the
            CARBOLATOR concept of water treatment.

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FULL-SCALE LABORATORY TESTS OF THE CARBOLATOR 35B

The following pesticide formulations were added to 400 gallons of tapwater held in a 500-gallon fiberglass cylindrical tank:

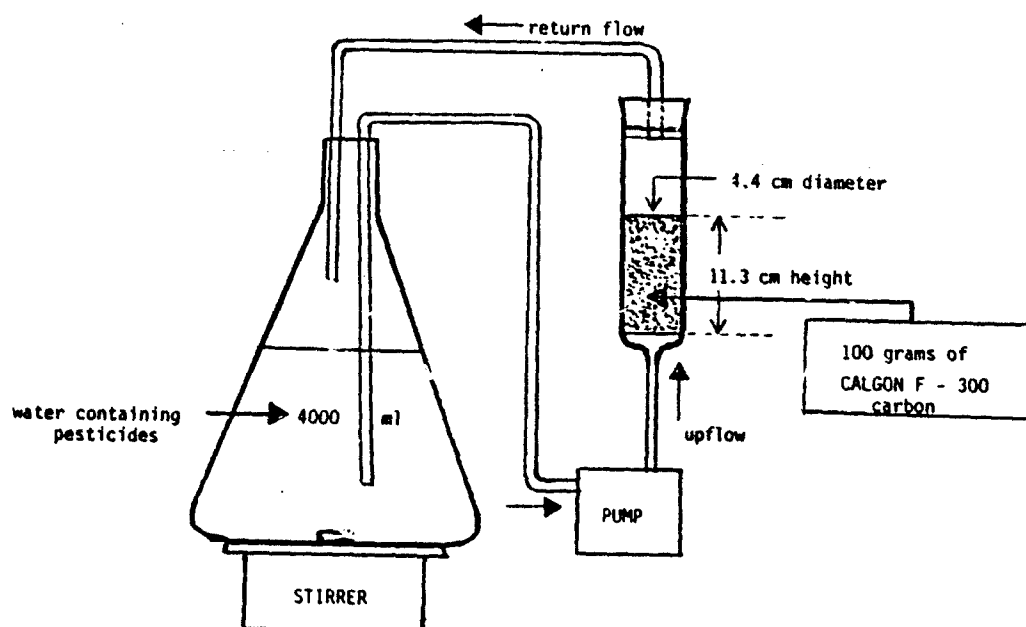|	Active Ingredient	Formulation Description
1.	Baygon (propoxur)	Baygon - 70% wettable powder, Chemagro Agricultural Division of Mobay Chem. Corp., Kansas City, MO
2.	Diazinon	Diazinon 4E, Crown Chemicals, Rockford, IL 47.7% diazinon emulsifiable concentrate, 4 lb/gal, 26.2% aromatic petroleum derivative, 26.0% inert ingredients.
3.	Malathion	91% Malation from a 55-gallon drum
4.	Dursban (chlorpyrifos)	Dursban M, 4 lb/gal, 41.2% Dursban, 29.5% petroleum derivative, 29.3% inert ingredients, Dow Chemical Co., Midland, MI
5.	2,4-D (low volatile ester)	TRANSVAAL-, 69.9% 2,4-dichlorophenoxyacetic acid - isooctyl ester, EPA 11687-4-AA.
6.	Ronnel (fenchlorphos)	DK-11 emulsifiable concentrate, 12.0% 0,0-dimethyl-0-(2,4,5-trichlorophenyl) phosphoro-thioate 11.1% 2,2-dichlorovinyl-dimethyl phosphate, 5% tetrachloroethylene, 11.5% Xylene, Stephenson Chemical Co., Inc., College Park, GA.
7.	Dimethoate	CYGON 2E, 23.4% dimethoate, 76.6% inert ingredients, B.G. Pratt Division, Gabriel Chemicals, LTD, Paterson, NJ

Three concentration levels of this mixture were used: 20 mg/L, 60 mg/L, and 100 mg/L of each of the active ingredients. Two porous polypropylene bags containing a total of 45 lb of Calgon F-300 activated carbon were rinsed in tapwater to remove carbon fines. This washed carbon was then loaded into the body of the CARBOLATOR (see Figure 3) and the top plate sealed. The contents of the 500-gallon synthetic waste tank were agitated by a 1/4 HP gear-driven stirrer with a shaft holding two 9-in diameter marine impeller blades. The contents of the tank were pumped through the bed of carbon in the CARBOLATOR, and the effluent returned to the tank. The flow rate was 6.4 gpm. Aliquots of 10 mL were taken at the inlet to the CARBOLATOR (to represent composition of tank contents) at known time intervals. All samples were analyzed by gas chromatography. Tables 4 through 6 present the change in concentration of each pesticide as a function of time at the three initial levels of 20 ppm, 60 ppm, and 100 ppm, respectively. Included in these tables are the theoretical concentrations that would be expected if a single pass through the

TABLE 4. PESTICIDE CONCENTRATION IN 400 GALLONS OF WATER DURING TREATMENT WITH CARBOLATOR 35B

Time (min)	Theoretical[a]	Baygon	Dimethoate	Diazinon	Ronnel	Malathion	Dursban	2,4-D (LVE)
0	20	20	20	20	20	20	20	20
10	17	-[b]	15.5	18.3	18.5	-	18.1	18.3
20	14.6	13.1	14.2	15.9	15.3	14.2	15.6	15.6
30	12.3	-	11.0	16.5	14.7	10.1	14.5	14.5
45	9.6	8.2	9.1	15.0	11.2	8.7	11.3	11.7
60	7.6	6.6	7.4	11.3	10.9	7.4	11.0	11.5
90	4.6	7.5	7.5	7.3	6.7	6.4	6.9	7.3
120	3.0	4.8	4.7	5.7	4.6	4.0	4.5	5.0
150	1.8	3.2	3.2	4.6	3.8	3.1	3.7	4.1
210	0.7	trace	2.9	3.5	2.3	2.8	2.2	2.5
230	0.5	ND[c]	2.3	2.4	1.8	2.4	1.7	2.2
320	0.12	ND	ND	1.2	0.8	1.9	0.8	1.2
360	0.06	ND	ND	1.1	0.6	1.7	0.7	0.7
420	0.025	ND	ND	1.0	0.5	1.9	0.4	0.5
520	0.01	ND	ND	0.8	0.4	1.2	0.4	0.5
840	10⁻⁴	ND	ND	0.2	0.1	1.0	0.03	0.05

a. Based on $\frac{C_t}{C_o} = e^{-Qt/V}$ where Q = 6.4 gallons/min and V = 400 gallons.

b. Not analyzed.

c. ND = not detectable by GC.

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TABLE 5. PESTICIDE CONCENTRATION IN 400 GALLONS OF WATER DURING TREATMENT WITH CARBOLATOR 35B

Time (min)	Theoretical[a]	Baygon	Dimethoate	Diazinon	Ronnel	Malathion	Dursban	2,4-D (LVE)
0	60	60	60	60	60	60	60	60
10	51	40	52	52	52	59	53	53
20	44	32	41	47	46	47	47	47
30	37	26	39	43	45	39	43	44
45	29	28	37	42	42	44	42	43
60	23	22	28	35	34	35	36	35
90	14	23	23	30	32	29	31	31
120	9	13	16	23	24	17	23	24
160	4.7	9	15	17	16	14	16	17
180	3.4	4	15	16	16	13	16	17
255		5	7	8	8	8	9	8
300	0.5	4.5	4	7	5.7	7	5.8	6
340	0.3	4	4	5.7	5.7	7	5.8	6
410		3	2.7	3.5	2.4	3.8	2.3	2.6
510	0.02	0.1	1.4	2.6	1.5	1.4	1.7	2.3
570		0.03	1.2	2.2	1.0	1.2	1.1	1.5
630	0.003	ND[b]	ND	1.5	0.7	0.8	0.7	1.0
810		ND	ND	1.1	0.4	0.6	0.4	0.7
1100		ND	ND	1.0	ND	ND	ND	ND

a. Based on $\frac{C_t}{C_o} = e^{-Qt/V}$ where $Q = 6.4$ gallons/min and $V = 400$ gallons.

b. ND = not detectable by GC.

TABLE 6. PESTICIDE CONCENTRATION IN 400 GALLONS OF WATER
DURING TREATMENT WITH CARBOLATOR 35B

Time (min)	Theoretical[a]	Baygon	Dimethoate	Diazinon	Ronnel	Malathion	Dursban	2,4-D (LVE)
0	100	100	100	100	100	100	100	100
10	85	94	95	94	97	92	89	86
20	73	85	81	77	87	89	75	74
30	62	79	78	75	84	73	72	63
45	48	72	68	60	55	60	64	65
60	38	65	62	54	47	54	59	69
90	24	48	46	35	34	36	39	45
120	15	42	40	46	55	44	52	54
180	5.6	30	31	46	62	38	52	52
300	0.8	18	18	30	44	23	37	38
360	0.3	15	16	24	38	19	32	33
450	0.07	12	12	19	32	15	28	30
620	5×10^{-3}	5	3	7	15	5	14	20
880		1	1	2	5	1.5	5	7
1100		0.4	0.5	1.5	5	1.0	5	10
1250		0.5	ND[b]	1.4	2	0.9	2.6	5.6

a. Based on $\dfrac{C_t}{C_o} = e^{-Qt/V}$ where Q = 6.4 gallons/min and V = 400 gallons.

b. ND = not detectable by GC.

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carbon bed were able to remove <u>all</u> of a pesticide from the water. These values are based on Equation 7, where V = 400 gallons, Q = 6.4 gpm and k = 1. In addition to the tabular presentation of these data, the log concentration was plotted against time for each pesticide. This is the graphical representation of Equation 7.

$$\log C_1/C_o = \frac{-kQt}{2.303V} \quad -$$

From the treatment data, the efficiency factor, k, can be determined. These plots are presented in Appendix A. The dashed line represents the decline in pesticide concentration if k = 1.0. The values of k were determined graphically from the plots shown in Appendix A for the 95 percent decrease in pesticide concentration in each of the three experiments. These values are presented in Table 7.

TABLE 7. VALUES OF k THAT WERE DETERMINED GRAPHICALLY FROM EXPERIMENTAL DATA COVERING 95 PERCENT REMOVAL OF THE PESTICIDE FROM WATER

Initial Pesticide Conc.	k Value						
	Baygon	Dimethoate	Diazinon	Ronnel	Malathion	Dursban	2,4-D(LVE)
20 mg/L	0.83	0.69	0.53	0.64	0.61	0.62	0.56
60 mg/L	0.81	0.47	0.44	0.43	0.43	0.43	0.40
100 mg/L	0.32	0.33	0.26	0.20	0.29	0.20	0.16

TESTING OF THE CARBOLATOR 35B UNIT AT FORT EUSTIS, VA

A preliminary test with the Fort Eustis wastewater showed that an in-line filter was needed for removal of suspended solids from the water before the waste passed into the CARBOLATOR. A drawing of the assembled apparatus is shown in Figure 9. As shown, water is taken from the bottom of the holding tank by a pump, P_1. The majority of the water passes back into the tank through line L_1. This keeps the contents of the tank constantly but not completely mixed. Part of the output of P_1 passes through a second pump, P_2, and then through a 20-inch Filterite[R] cartridge filter (F) in a polycarbonate housing. The filtered water then passes into the bottom of the CARBOLATOR which contains a bed of granular carbon (Calgon F-300) held in two porous polypropylene bags. The carbon-filtered water is returned to the tank through a flexible line, L_2. All water samples are returned to the laboratory and analyzed by gas chromatography.
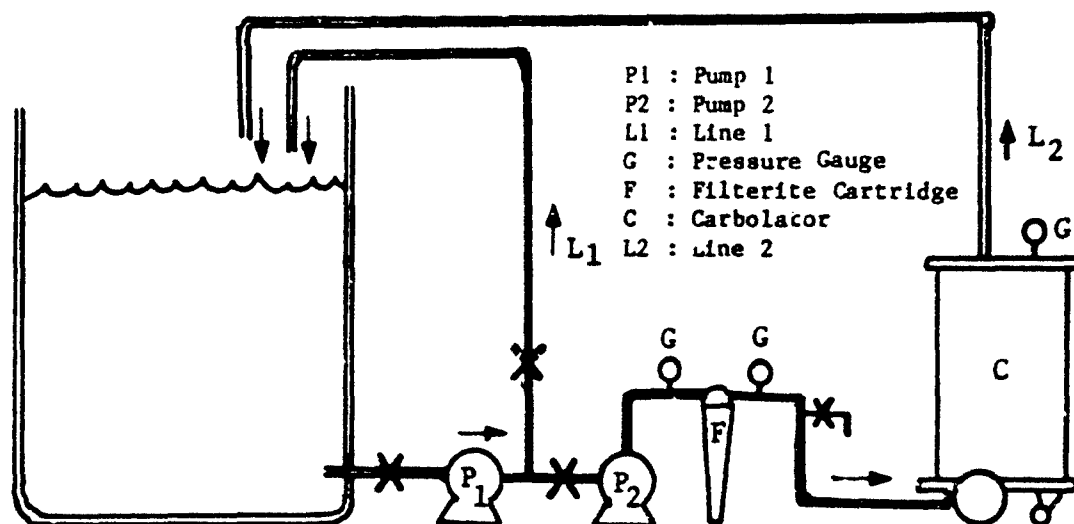
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Figure 9. Schematic drawing of CARBOLATOR system tested at Fort Eustis, VA.

The first field test of the CARBOLATOR treatment system was made in July 1981. On arrival at Fort Eustis, VA, this system (Figure 9) was assembled and connected to the wastewater tank containing about 600 gallons of water. On-site analysis of the waste by TLC showed the presence of malathion, dimethoate, and baygon with traces of diazinon and dursban. On the following day, water was passed through the system (30 lb Calgon F-300) and returned to the waste tank. As the cartridge filters (2-micron size) became fouled (and the flow diminished) they were replaced. During the first 9 hours of operation, the gauge pressures on each side of the cartridge filter were recorded and the flow (output) from the CARBOLATOR monitored. Table 8 presents the pressure and flow characteristics of this test. The cumulative volume of water passing through the CARBOLATOR was determined by graphic integration of a flow versus time plot. The system was allowed to operate unattended overnight, and no problems were encountered. After 24 hours of treatment, no pesticides could be detected in the water by the on-site TLC analysis. The average flow was 6.1 gpm for the full operation.

Gas chromatographic analysis of samples taken from the waste tank showed a steady decline in all three pesticides from the water. The initial concentrations of pesticides found in the wastewater were:

	mg/L
Dimethoate	48.0
Malathion	33.5
Baygon	2.5
Diazinon	0.5

TABLE 8. PRESSURE AND FLOW CHARACTERISTICS OF THE CARBOLATOR
FILTRATION SYSTEM DURING THE FIELD TEST OF JULY 1981

| Time | Hours of Operation | Pressure Across Cartridge Filter | | Flow (gpm) from CARBOLATOR | Comments | Cumulative Gallons Processed |
		Inlet (psi)	Exit (psi)			
0710	0.00	22.0	9.0		Turn-on	0
0715		25.0	2.0		Change filter	
0720		17.0	13.5			
0725	0.25	21.0	10.5	8.13		
0730		24.0	3.5	3.45		
0735		25.0	1.5	1.32	Change filter	
0740	0.50	18.5	13.5	9.11		
0745		20.5	11.0	7.43		170
0750		23.0	7.0	5.94		
0755	0.75	24.0	3.5	3.45		
0800		25.0	2.0	1.84		280
0805		26.0	1.5	1.08	Change filter	
0810	1.00	18.5	13.5	9.16		
0815		20.0	12.0	8.51		
0820		23.0	7.5	6.12		
0825	1.25	24.0	3.5	3.15		
0830		25.0	2.0	1.62		
0835		26.0	1.5	0.93	Change filter	
0840	1.50	18.0	13.5	9.21		500
0850		21.0	10.0	7.47		
0900		24.5	2.0	2.09		625
0910	2.00	26.5	1.0	0.55	Change filter	
0915		18.0	13.5	9.13		683
0925		19.5	12.0	7.93		753
0935		22.0	9.0	6.99		840
0945		24.5	5.0	4.50		910
0955	2.75	25.0	3.0	1.94		952
1005		26.0	1.5	0.94	Change filter	975
1010	3.00	18.0	13.5	9.77		
1025		19.5	12.0	8.83		
1040	3.50	21.5	9.0	6.78		1,200
1055		24.0	5.0	5.11		1,313
1110	4.0	24.0	2.0	2.66		1,380
1125	4.25	25.5	1.5	1.35	Change filter	
1130	4.33	18.0	14.0	9.41		
1230	5.33	20.0	11.5	8.14		1,960
1300	5.83	21.0	10.0	7.17		2,190
1330	6.33	22.5	8.0	6.67		2,424
1400	6.83	23.0	7.0	6.18		2,618
1430	7.33	24.0	6.0	5.45		2,795
1500	7.83	25.0	5.0	5.05		
1525		25.0	4.0	4.53	Change filter	
1530	8.33	8.0	7.5	7.00		3,100
0710[a]	24.00	8.5	8.0	6.55	2nd day	9,465

a. Following day.

Table 9 shows the concentration of pesticides in the holding tank as a function of time. The plot of log pesticide concentration versus time are shown in Appendix B.

A second field test was made in September 1981. The set-up was identical to that shown in Figure 9. In this trial, 410 gallons of wastewater (20°C) were processed with the CARBOLATOR system (40 lb Calgon F-300 were used). The system was operated over a 3-day period for a total of 20 hours. The cartridge filter was charged with a 10-micron cotton-wound filter tube in this test. Again, on-site TLC analysis was used to determine the composition of the waste. Samples were collected between the pump and in-line filter and returned to the laboratory for GC analysis. The composition of the waste prior to treatment was:

	mg/L
Malathion	81.7
Baygon	40.8
Dursban	18.7
Dimethoate	17.4
Diazinon	10.1
2,4-D(LVE)	6.4

The flow and pressure characteristics of the system were monitored during the water processing (Table 10). The results of GC analyses of the water as a function of time are shown in Table 11.

RESULTS OF LABORATORY-SIMULATION OF CARBOLATOR

Table 12 shows the changes in concentration of seven different pesticides present in the test water undergoing recirculation through 100 grams of Calgon F-300 granular activated carbon (see Figure 8). It can be seen that 100 grams of carbon were able to remove all of the pesticides from 4 liters of water within 8 hours under the given conditions. Further, both baygon and dimethoate closely follow the theoretical exponential curve indicating that these substances must be absent in the effluent from the carbon column. The efficiency of pesticide removal appears to be:

Decreasing efficiency

baygon>dimethoate>malathion>diazinon>ronnel>dursban>2,4-D(LVE)

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TABLE 9. PESTICIDE CONCENTRATION IN FORT EUSTIS WASTEWATER AS CARBOLATOR
TREATMENT PROGRESSED. SAMPLES TAKEN BETWEEN PUMP AND IN-LINE FILTER
SEPTEMBER 1981 FIELD TEST

Time (min) in Operation	Concentration of Pesticides (mg/L)					
	Malathion	Baygon	Dursban	Dimethoate	Diazinon	2,4-D (LVE)
0	81.7	40.8	18.7	17.4	10.1	6.4
9	8.5	37.3	16.2	15.5	7.7	5.9
24	--[a]	34.8	16.6	14.5	8.6	5.1
55	6.7	30.7	14.9	13.3	7.2	5.3
69	0.7	27.6	12.5	11.2	5.8	4.5
85	ND[b]	24.6	11.8	9.9	5.6	3.8
100	ND	22.1	10.8	8.7	4.8	3.9
115	ND	21.2	11.3	8.3	5.3	3.8
140	ND	19.8	11.2	7.8	4.5	3.7
160	ND	18.2	8.8	6.8	4.2	3.4
180	ND	13.8	8.1	5.9	4.1	3.5
205	ND	9.0	7.2	5.1	3.4	3.5
240	ND	8.5	5.8	4.0	2.6	2.5
300	ND	5.8	5.3	2.6	1.7	2.0
330	ND	4.5	3.7	2.2	1.8	1.5
360	ND	3.3	3.4	1.7	1.4	1.3
420	ND	2.3	3.2	1.1	0.9	1.4
480	ND	1.2	2.9	0.6	0.5	1.1
540	ND	0.9	2.1	ND	0.05	0.7
618	ND	0.5	1.7	ND	0.01	0.5
720	ND	0.3	0.9	ND	0.02	0.1
780	ND	0.2	0.6	ND	ND	0.2
840	ND	ND	0.8	ND	ND	0.2
1,200	ND	ND	0.3	ND	ND	0.1

a. Not analyzed.
b. ND = not detectable by GC.

TABLE 10. PRESSURE AND FLOW CHARACTERISTICS OF THE CARBOLATOR FILTRATION SYSTEM DURING THE FIELD TEST OF SEPTEMBER 1981

Time	Hours of Operation	Pressure Across Cartridge Filter		Flow (gpm) from CARBOLATOR	Comments
		Inlet (psi)	Exit (psi)		
0925	0	-	-	-	Start, Day 1
0937	0.2	10.1	6.0	6.12	Sample port clogged restart at 0944
0949	0.28	12.0	5.0	5.47	
1000		15.0	4.0	4.39	
1006	0.56	16.0	4.0	3.63	Change filter, stop for repairs, start again 1120
1120	0.56	15.0	12.0	8.91	
1133	0.77	16.0	11.0	8.32	
1142		18.0	9.5	7.52	
1155	1.14	21.0	7.5	6.43	
1202		23.0	6.0	5.57	
1206	1.32	20.0	4.5	4.27	
1217		22.0	3.5	3.32	
1225	1.64	23.5	2.5	2.82	
1235		24.0	2.5	-	Change filter start again 1238
1250	2.06	6.5	5.0	4.65	Turn off pump #2 (P$_2$)
1310	2.38	7.0	5.0	4.40	
1320		7.5	4.5	4.27	Turn P$_2$ back on
1330	2.72	10.5	6.2	5.50	
1355		12.5	6.0	5.47	Boost pressure to P$_2$
1410		16.0	6.5	5.72	
1430	2.72	17.0	6.0	5.33	
1445	2.97	18.0	5.5	5.03	Boost input to P$_2$
1447		22.0	6.5	5.88	
1500	3.22	23.0	6.0	-	
1530	3.72	24.0	5.0	4.42	Shutdown for day. Replace filter
0630	3.72	8.5	7.0	6.00	Start Day 2
0700	4.22	8.5	7.0	6.00	
0730	4.72	9.0	7.0	6.06	
0800	5.22	9.5	7.0	5.89	
0900	6.22	10.0	7.0	6.00	
0930	6.72	10.5	7.0	5.89	
1030	7.72	11.0	7.0	5.83	
1150	9.05	11.5	6.5	5.78	Boost input to P$_2$
1155		13.0	7.0	6.30	
1230	9.72	13.0	7.5	6.24	
1330	10.72	14.0	7.0	5.94	
1415		15.0	7.0	5.72	Boost input to P$_2$
1430	11.72	16.0	7.5	6.00	
1530	12.72	17.0	7.0	5.83	Shutdown, change filter
0630	12.72	9.0	7.5	6.12	Start Day 3
0715	13.47	9.0	7.5	6.12	
0830	14.72	9.0	7.5	6.12	
1330	19.72	10.0	7.0	5.80	TLC shows no pesticides
1400	20.22	10.0	7.0	5.80	End Test

TABLE 11. PESTICIDE CONCENTRATION IN FORT EUSTIS WASTEWATER AS
CARBOLATOR TREATMENT PROGRESSED[a]

Time (min) in Operation	Concentration of Pesticides (mg/L)					
	Malathion	Baygon	Dursban	Dimethoate	Diazinon	2,4-D (LVE)
0	81.7	40.8	18.7	17.4	10.1	6.4
9	8.5	37.3	16.2	15.5	7.7	5.9
24	-[b]	34.8	16.6	14.5	8.6	5.1
55	6.7	30.7	14.9	13.3	7.2	5.3
69	0.7	27.6	12.5	11.2	5.8	4.5
35	ND[c]	24.6	11.8	9.9	5.6	3.8
100	ND	22.1	10.8	8.7	4.8	3.9
115	ND	21.2	11.3	8.3	5.3	3.8
140	ND	19.8	11.2	7.8	4.5	3.7
160	ND	18.2	8.8	6.8	4.2	3.4
180	ND	13.8	8.1	5.9	4.1	3.5
205	ND	9.0	7.2	5.1	3.4	3.5
240	ND	8.5	5.8	4.0	2.6	2.5
300	ND	5.8	5.3	2.6	1.7	2.0
330	ND	4.5	3.7	2.2	1.8	1.5
360	ND	3.3	3.4	1.7	1.4	1.3
420	ND	2.3	3.2	1.1	0.9	1.4
480	ND	1.2	2.9	0.6	0.5	1.1
540	ND	0.9	2.1	ND	0.05	0.7
618	ND	0.5	1.7	ND	0.01	0.5
720	ND	0.3	0.9	ND	0.02	0.1
780	ND	0.2	0.6	ND	ND	0.2
840	ND	ND	0.8	ND	ND	0.2
1,200	ND	ND	0.3	ND	ND	0.1

a. Samples taken between pump and in-line filter – September 1981 field test.
b. Not analyzed.
c. ND = not detectable by GC.

TABLE 12. CHANGE IN CONCENTRATION OF SEVEN PESTICIDES DURING SMALL-SCALE SIMULATION OF THE CARBOLATOR WATER TREATMENT CONCEPT

Time (min)	Theoretical[a]	Baygon	Dimethoate	Diazinon	Ronnel	Malathion	Dursban	2,4-D (LVE)
			Concentration in mg/L					
0	100	100	100	100	100	100	100	100
5	69	75	63	88	80	83	89	87
10	47	50	51	77	72	75	84	79
15	33	36	37	72	68	68	82	79
20	22	26	27	64	64	56	72	73
30	11	18	15	58	54	44	72	66
40	5	3	10	48	49	34	64	59
50	2	ND[b]	8	40	41	25	57	57
60	1	ND	4	25	32	17	47	43
80	0.2	ND	3	15	24	9	38	32
100	0.05	ND	1	11	15	4	29	27
120	0.01	ND	1	5	11	2	23	21
180		ND	ND	0.6	4	ND	10	11
360		ND	ND	0.2	0.5	ND	1	3
465		ND	ND	ND	ND	ND	ND	1

a. Based upon $\dfrac{C_t}{C_o} = e^{-Qt/V}$ where Q = 300 mL/min and V = 4,000 mL.

b. ND = not detectable by GC.

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Since some pesticides are not amenable to gas chromatographic analysis in the presence of other pesticides, it is possible to study such compounds in water alone. Two such compounds are the 2,4-D diethylamine salt and chlordane. Figure 10 shows that the 2,4-D salt is removed from water by carbon with high efficiency. Chlordane removal, as shown in Figure 11, is very slow.

CAPACITY OF CALGON F-300 FOR PESTICIDE ADSORPTION

It is of great importance to know what mass of pesticides can be adsorbed from water by a given quantity of Calgon F-300 granular carbon. To determine this, 20 grams of Calgon F-300 were gently shaken with 300 mL of water containing four pesticides (suspensions of the emulsifiable concentrates of diazinon, baygon, dursban, and malathion at concentrations of 200 mg/L each).

The 20 grams of carbon and 300 mL of suspension were placed in a 600-mL beaker and mixed with a metal paddle in a jar-test apparatus. Aliquots of the solution were removed at 5 min, 10 min, 30 min, 1 hr, 2 hr, and 24 hr. After 24 hr the supernatant liquid was decanted from the 20 grams of carbon. This same carbon was then challenged again with 300 mL of a fresh aqueous suspension of pesticides, and samples were taken for analysis. This same 20 grams of carbon was used this way from 1 day to another for a total of 11 times. The results of these multiple challenges to the same carbon are presented in Table 13. It can be seen that even after nine repetitions, the 20 grams of carbon is still able to efficiently remove the pesticides from the water. At this point, the carbon is holding about 10 percent of its weight in pesticides. Beyond this, the ability of the carbon to bind further amounts of pesticides declines. On the 11th challenge, the carbon has adsorbed 12.5 percent of its weight in pesticides, which appears to be the limit.

LEACH TESTING OF THE PESTICIDE-CONTAMINATED CARBON

The use of activated carbon to adsorb pesticides from wastewaters transfers the pollutant from a large volume to a solid, dry, compact form. The ultimate disposal of this spent carbon must be considered. Since the Army pesticide facilities are generators of relatively small quantities of waste, the most practical method would be disposal of the spent carbon in landfills. This may be done if the material can be shown not to be a "hazardous waste" as defined by the Environmental Protection Agency (EPA). A test has been published by EPA (Federal Register, Rules and Regulations, Vol. 45, No. 98, May 19, 1980) to measure the degree to which hazardous pollutants may leach from a solid waste in a landfill. Two spent carbons, generated during laboratory CARBOLATOR evaluations with Calgon F-300 granular activated carbon and synthetic wastewaters laden with pesticides, were subjected to this EPA leaching test.

A quantity of air-dried spent carbon (25 g) containing a known amount of pesticide was mixed with 400 mL of glass-distilled water adjusted to pH 5 with acetic acid. This was placed in a screw cap bottle and shaken vigorously on a wrist-action shaker for 24 hours. After 24 hours of agitation, the contents of the flask was filtered through a 0.45 micron filter and diluted to 500 mL with water. This solution was extracted with CH_2Cl_2 (three 25-mL portions), the CH_2Cl_2 extract concentrated in a Kuderna-Danish apparatus, and the concentrated CH_2Cl_2 analyzed for pesticides by gas chromatography using a nitrogen-phosphorus (NP) detector. (An NP detector is used in order to measure pesticides in water when concentration is below 1 mg/L.) Table 14 shows the
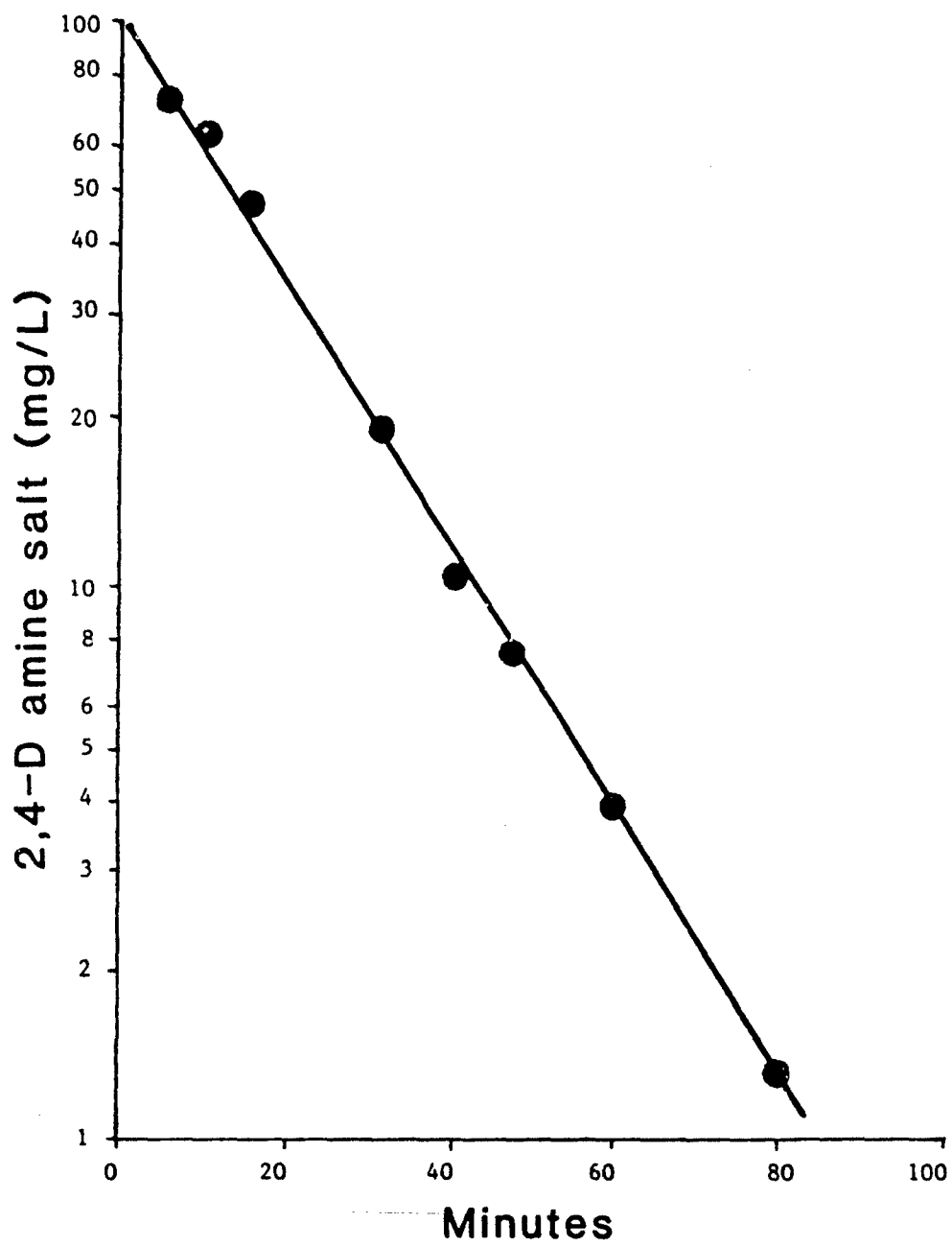
Figure 10. Removal of the diethylamine salt of 2,4-D from 4 liters of water using the apparatus shown in Figure 9. Flow rate was 222 mL/min. The exponential decline matches the theoretical loss.
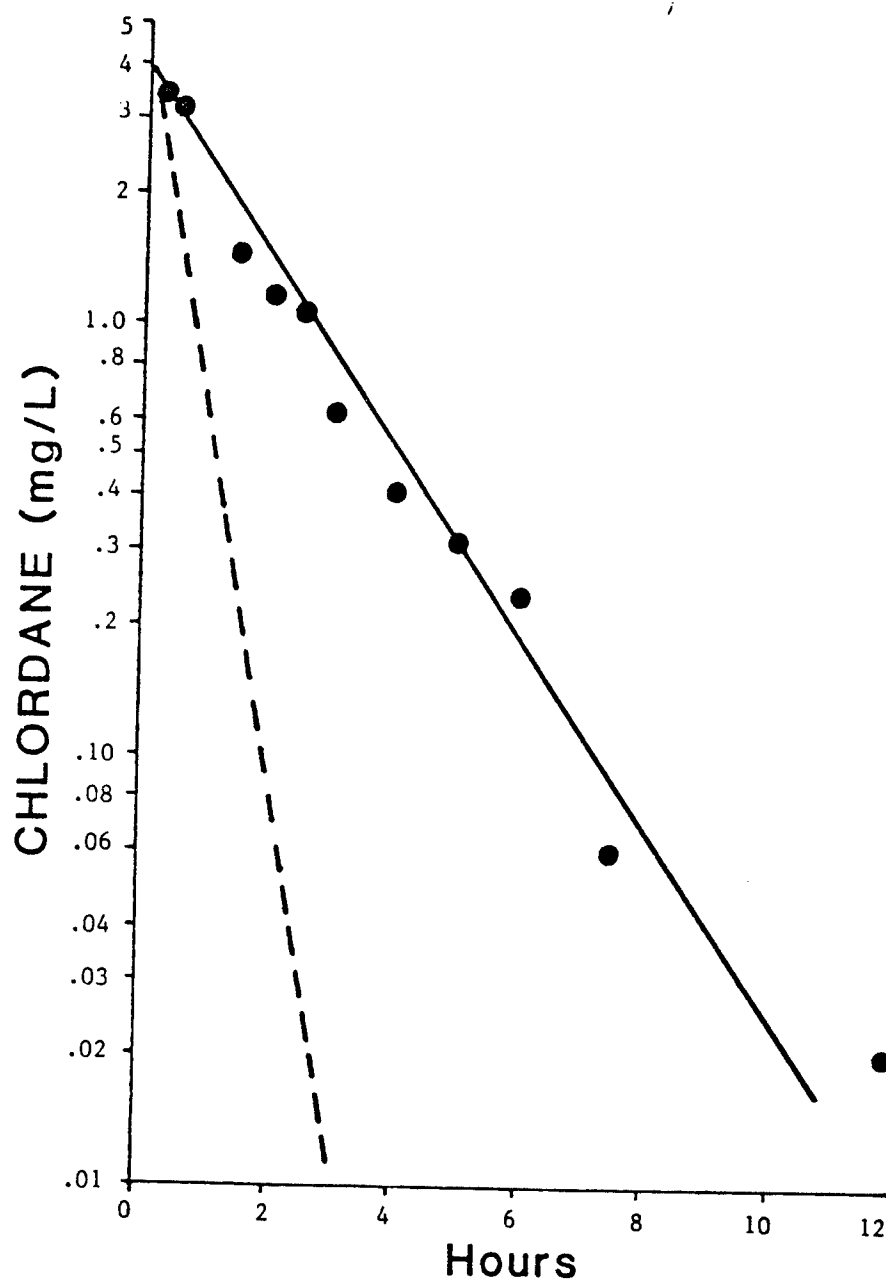
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Figure 11. Removal of chlordane from 4 liters of water using the
apparatus shown in Figure 9. Flow rate was 214 mL/min.
The dashed line is the theoretical loss based on
equation 1 where k = 1.0.

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TABLE 13. EXPERIMENT TO DETERMINE THE ADSORPTIVE CAPACITY OF CALGON F-300 GRANULAR ACTIVATED CARBON

			% Pesticide Removal After:						Cumulative Adsorption of Active Ingredient (grams of total pesticides per
Date	Challenge	Pesticide	5 Min	10 Min	30 Min	1 Hr	2 Hr	24 Hr	100 grams carbon X 100) (%)
2/6	1st	BAY	86	96	99	100	100	100	
		MAL	60	86	99	99	100	100	1.2
		DIAZ	53	80	99	100	100	100	
		DURS	45	70	96	98	100	100	
2/7	2nd	BAY	70	86	95	99	94	95	
		MAL	20	83	90	—	99	100	2.3
		DIAZ	7	55	86	95	95	95	
		DURS	38	40	70	83	70	70	
2/8	3rd	BAY	54	64	88	96	98	98	
		MAL	32	57	82	98	99	99	3.5
		DIAZ	24	37	90	94	95	95	
		DURS	20	32	80	86	—	88	
2/11	4th	BAY	45	57	62	90	95	100	
		MAL	5	40	69	95	96	100	4.6
		DIAZ	5	36	80	95	94	97	
		DURS	—	25	70	90	86	85	
2/13	5th	BAY	44	48	64	79	93	99	
		MAL	55	55	78	79	88	92	5.8
		DIAZ	30	40	90	94	56	97	
		DURS	35	38	89	96	—	94	
2/14	6th	BAY	24	40	47	70	85	100	
		MAL	27	74	85	95	96	98	7.0
		DIAZ	30	60	87	94	96	100	
		DURS	20	55	70	84	87	92	
2/15	7th	BAY	—	—	—	—	—	—	
		MAL	—	—	—	—	—	—	8.5
		DIAZ	—	—	—	—	—	—	
		DURS	—	—	—	—	—	—	
2/19	8th	BAY	25	30	45	48	—	96	
		MAL	36	50	70	89	—	97	9.4
		DIAZ	37	40		90	—	97	
		DURS	25	32	60	83	—	98	
2/20	9th	BAY	25	29	30	42	70	—	
		MAL	46	47	59	83	93	—	10.4
		DIAZ	39	38	46	79	91	—	
		DURS	30	27	37	72	77	—	
2/21	10th	BAY	25	25	25	—	—	80	
		MAL	42	60	80	—	—	89	11.4
		DIAZ	38	50	74	—	—	90	
		DURS	29	28	73	—	—	82	
2/22	11th	BAY	7	10	8	18	—	75	
		MAL	8	25	65	75	88	89	12.5
		DIAZ	23	31	54	75	39	89	
		DURS	6	19	53	69	83	82	

analysis of leachates from two spent carbons obtained from CARBOLATOR tests. One carbon is a representative sample of the 45 lb of Calgon F-300 used in cleaning 400 gallons of water at the 200 mg/L per pesticide. The second carbon is a similar sample from the experiment at the 60 mg/L level. It is evident that the equilibrium concentration of pesticides in the leachate is very low for both spent carbons.

TABLE 14. LEACH TEST OF SPENT CARBON FROM CARBOLATOR

April 28 Run - 6 Pesticides Pesticides 1.8% by Weight			April 21 Run - 7 Pesticides Pesticides 5.4% by Weight		
Leachate after 24 Hours			Leachate after 24 Hours		
Dimethoate		0.4 ppb	Dimethoate		4.0 ppb
Baygon		0.1 ppb	Baygon		8.0 ppb
Ronnel	below	0.2 ppb	Ronnel	below	0.2 ppb
Malathion	below	0.3 ppb	Malathion	below	0.3 ppb
Diazinon	below	0.1 ppb	Diazinon	below	0.1 ppb
Dursban	below	0.2 ppb	Dursban	below	0.2 ppb
			2,4-D (LVE)	below	10 ppb

DISCUSSION

The CARBOLATOR 35B system successfully removed seven pesticides from 400-gallon batches of synthetic wastewater. Even at the highest concentration (100 mg/L per pesticide), 99 percent of all baygon and dimethoate; 97 percent of all diazinon, ronnel, and malathion; and 95 percent of the dursban and 2,4-D(LVE) were removed in 21 hours with only 45 lb of granular carbon. The efficiency of removal differed among the seven pesticides, but always followed the same pattern. The removal efficiency appears to be:

increasing affinity for carbon
baygon > dimethoate > malathion > diazinon = ronnel > dursban = 2,4-D(LVE)

Of this group of pesticides, baygon and dimethoate follow most closely the theoretical exponential decline in concentration. It can be seen in Table 7 that the calculated k values decrease for every pesticide as its initial concentration increases. In no case did the k value reach 1.0 for any pesticide.

The first field test of the CARBOLATOR 35B carbon filtration system was conducted without any difficulties. The three major pesticides in the waste (dimethoate, malathion, and baygon) declined exponentially over the 8-hour period of observation. In the laboratory tests, both baygon and dimethoate were found to follow theoretical exponential decline; this was not observed in this first field test. The low level of diazinon (0.5 mg/L) in the wastewater did not show the expected exponential decline. It is possible that this low level was seen throughout the first 8 hours because diazinon was being

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continuously released from material deposited at the bottom of the tank. Nevertheless, after 24 hours of treatment all pesticides were below the limit of detection.

The second field test was also successful. The plots in Appendix C show definite exponential decline in pesticide concentrations. These declines were slower than the theoretical decline that would be expected based on the flow rate and volume of wastewater. The rapid loss of malathion (more rapid than theoretical, Table 11) was due to the heterogeneity of the waste. It was observed during the first few minutes of operation that a heavy oil had accumulated in the cartridge filter housing; this was apparently undissolved malathion that had been at the bottom of the holding tank. It was revealed later, that on the day before arrival for this test, an empty 55-gallon drum of 95 percent malathion was rinsed into the sump. This immiscible malathion was transferred to the holding tank by the sump pump. This insoluble material was pumped directly into the carbon bed (where it was retained) at the start of the operation. The aqueous phase of the waste contained very little dis-solved malathion. The overall test gave a processed water with no detectable malathion, baygon, dimethoate, or diazinon. At the termination of this test (20 hours), the levels of dursban and 2,4-D ester were 0.3 mg/L and 0.1 mg/L, respectively. Based on previous results, continued operation beyond 20 hours would have undoubtedly brought these levels to their limits of detection.

In both of these field tests, the application of thin-layer chromatography was considered to be essential for characterizing the pesticides in the water and in monitoring the progress of their removal by the carbon filtration system.

The ability to simulate the CARBOLATOR treatment system in the laboratory provides a tool to predict the behavior of the full-scale system in the field. With the apparatus shown in Figure 8, the adsorptive behavior of any pesticide with any granular activated carbon in water can be measured. Sev-eral pesticides may be compared simultaneously under a given set of parameters such as carbon type, flow rate, loading rate, temperature, and carbon bed geometry. Moreover, these parameters can be varied while the aqueous phase is held constant.
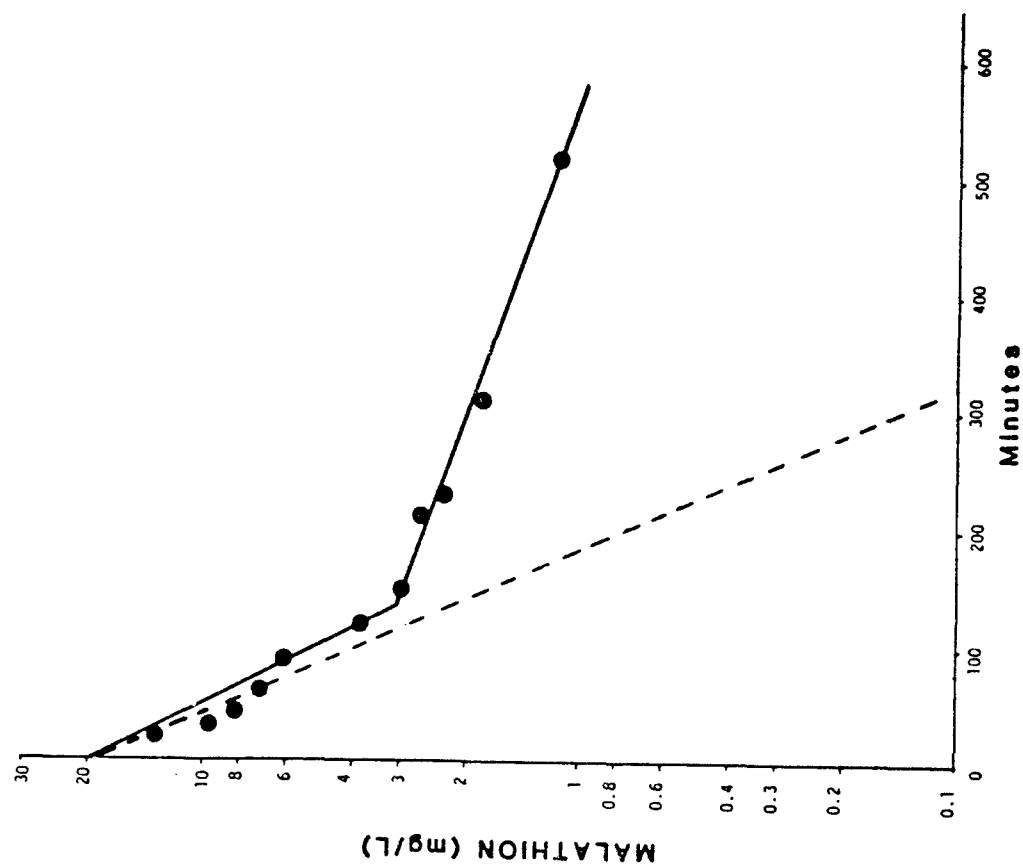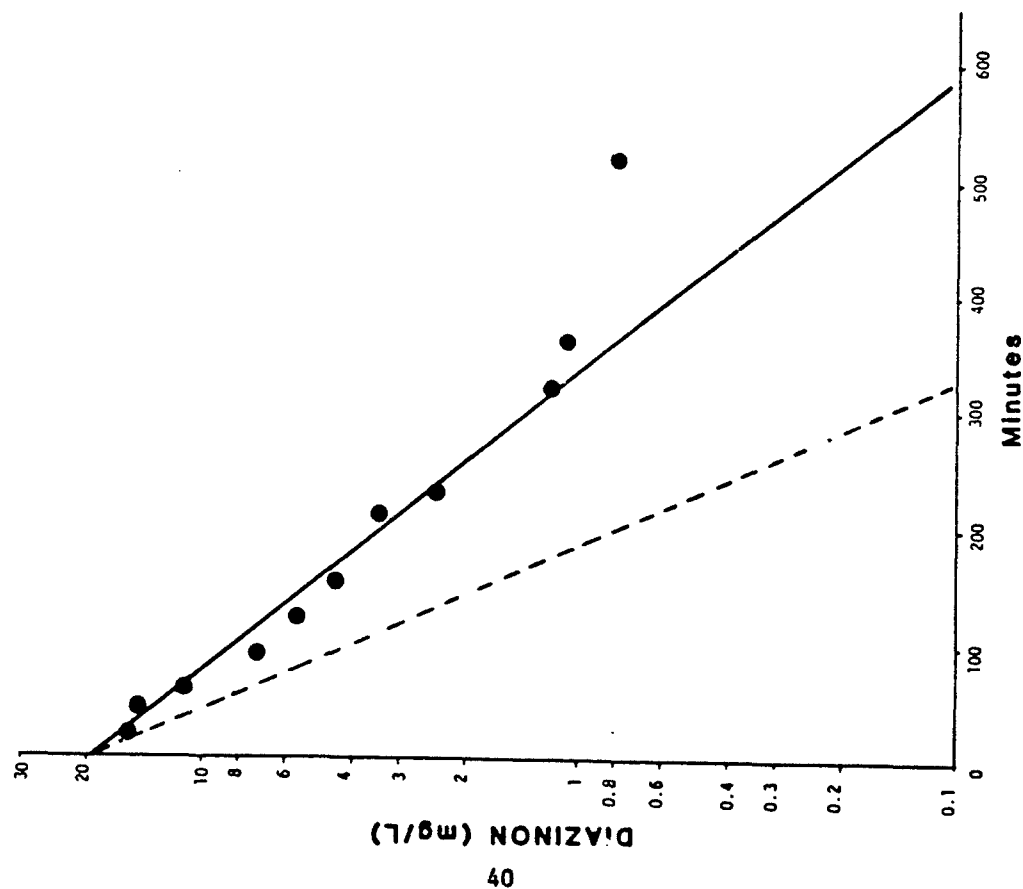
CONCLUSIONS AND RECOMMENDATIONS

1. Pesticide-laden wastewaters generated at US Army Pest Control facilities can be successfully treated by carbon filtration through a CARBOLATOR 35B[R] treatment system used in a recirculation mode. A pound of Calgon F-300 can retain a maximum of 0.1 lb pesticide.

2. The entire system can be assembled from commercial items at a capital cost of about $3,000.

3. Waters containing baygon, diazinon, dimethoate, dursban, ronnel, malathion, 2,4-D isooctyester and mixtures thereof, are amenable to this treatment method. Laboratory-scale simulations indicate that 2,4-D diethylamine salt, parathion, carbaryl, and chlordane may also be removed from water by this method.

4. With the exception of chlordane, 99 percent of all pesticides described above can be removed from a 400-gallon batch of water having an initial concentration of 420 mg/L total pesticides in 24 hours, when the CARBOLATOR is charged with 45 lb of Calgon F-300 carbon and operated 6.4 gpm at ambient temperature.

5. Thin-layer chromatography (TLC) is a simple, cheap, and valuable tool for characterizing a wastewater on-site, monitoring the progress of treatment, and assessing the quality of product water.

6. A spent carbon containing 5.4 percent pesticides by weight shows very little leaching of pesticide into water after a 24-hour leach test. The equilibrium concentration of pesticides in the leachate is in the 1-10 μg/L range.

7. The bench-scale model of the CARBOLATOR allows one to predict the behavior of various carbons that could be used in a filtration system as well as the behavior of pesticides other than those studied in this work.

8. Recommend that all US Army pest control facilities that have a problem with pesticide-wastewater disposal consider carbon-filtration as described above for the effective treatment of these wastes prior to discharge or reuse of these waters. A schematic drawing describing the components of the treatment train and showing their assemblage is given in Appendix D.
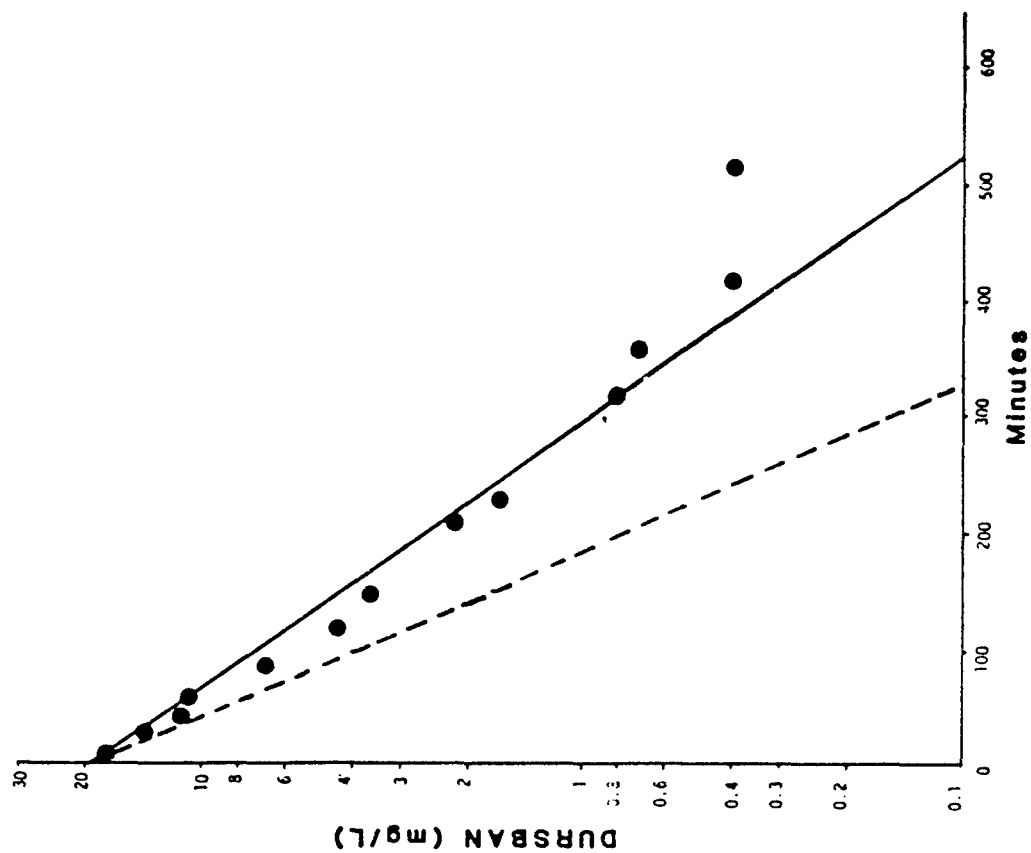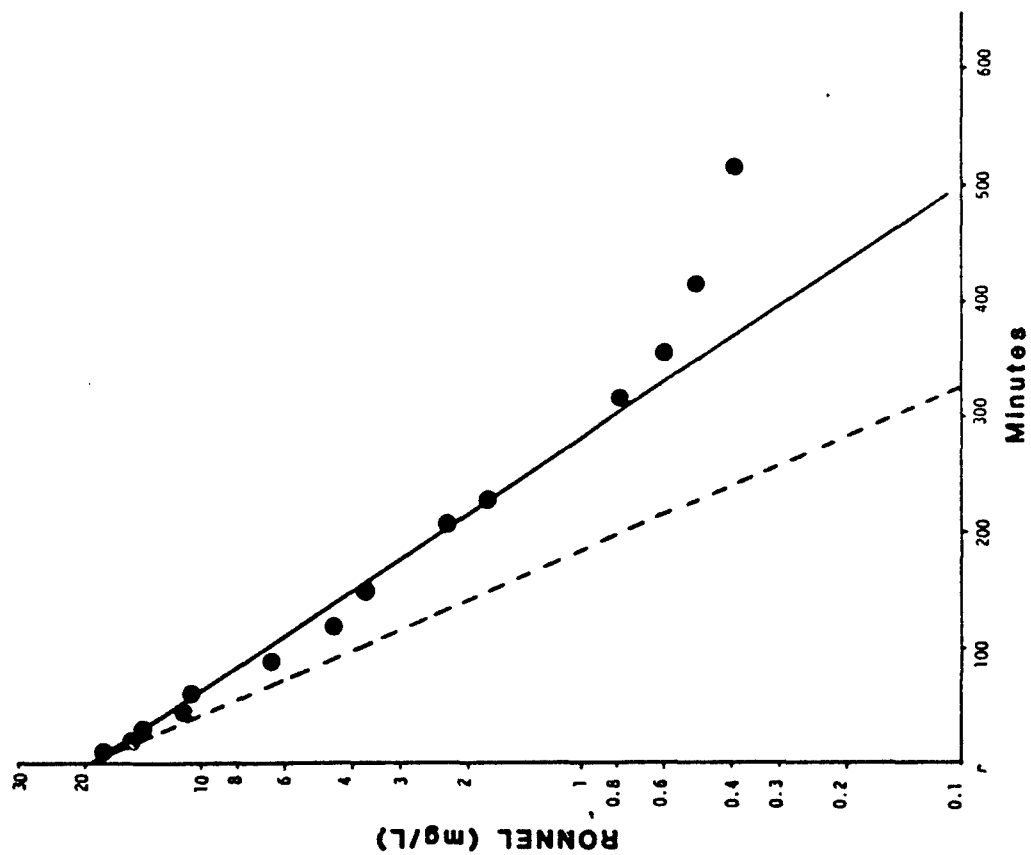
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APPENDIX A

Concentration of pesticides in 400 gallons of synthetic wastewater undergoing carbon filtration with the CARBOLATOR under laboratory testing. These plots represent trials at the 20 mg/L, 60 mg/L and 100 mg/L levels. The dashed line indicates the theoretical decline in concentration based on the complete removal of pesticide during a single pass at the given volume and flow rate.
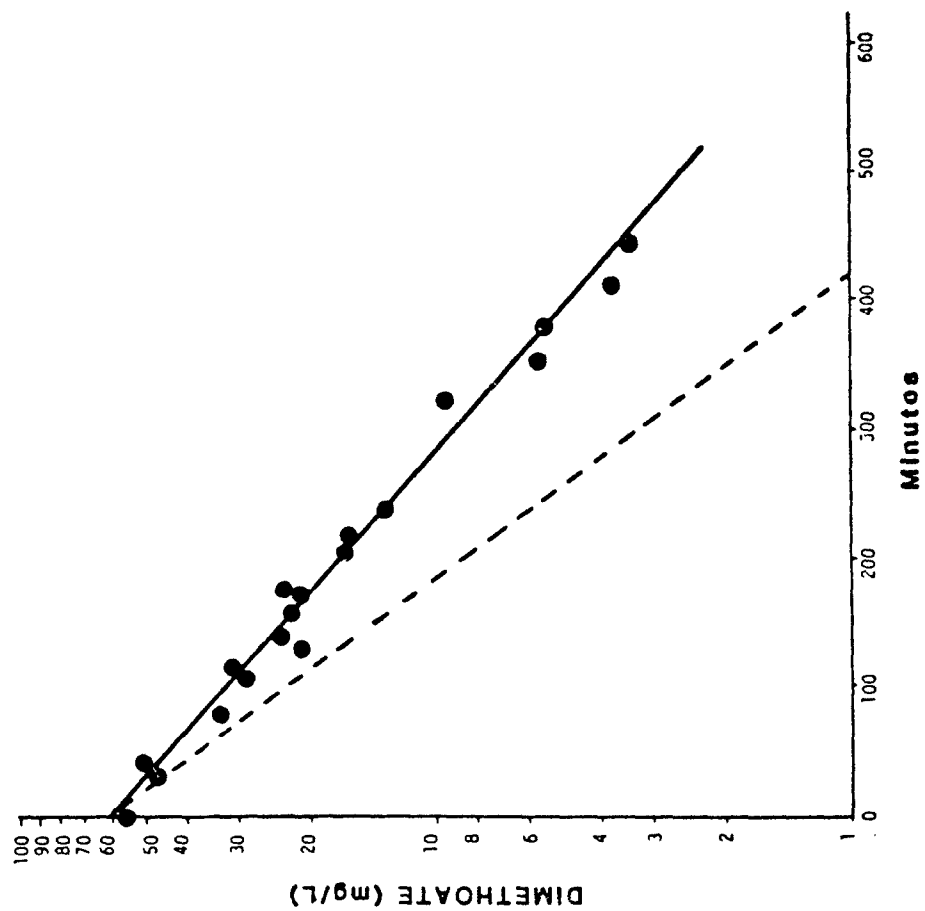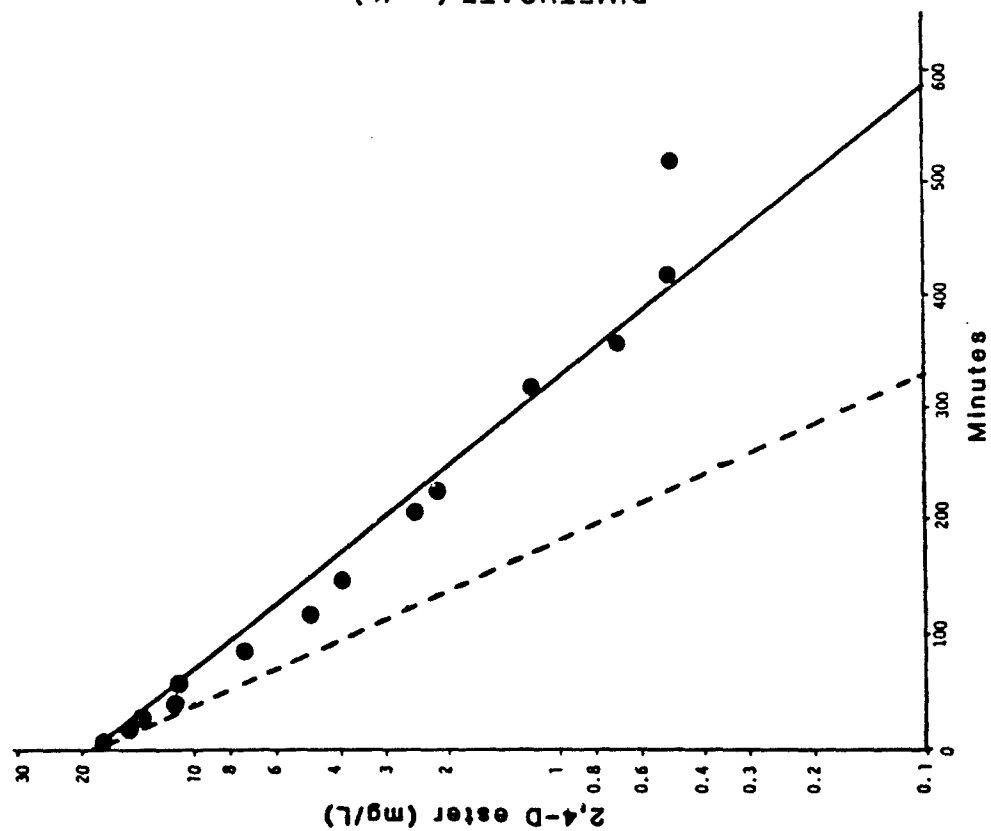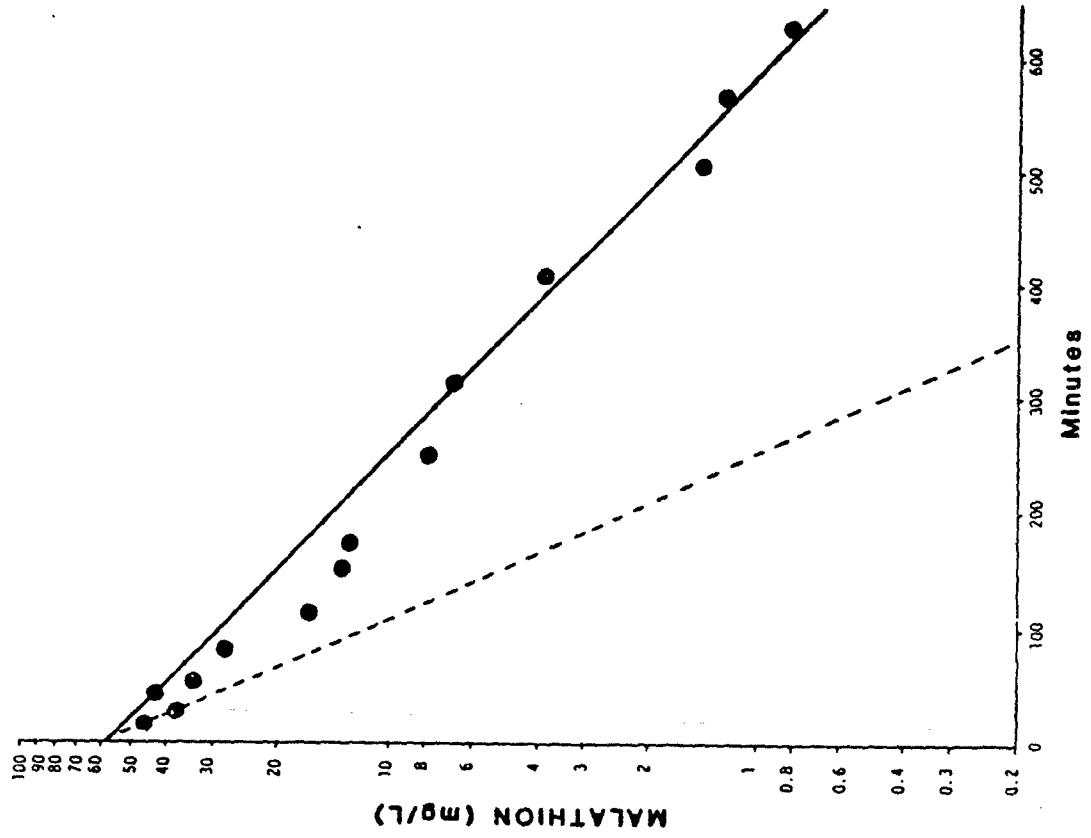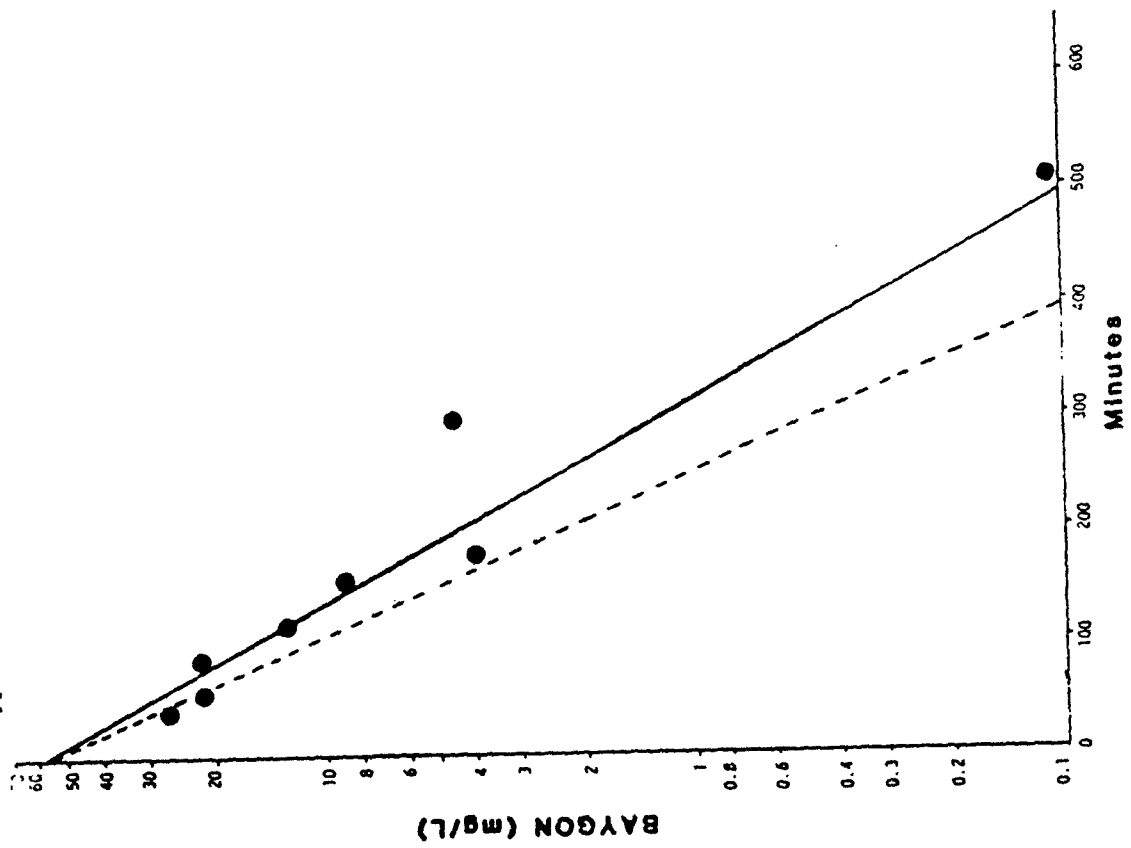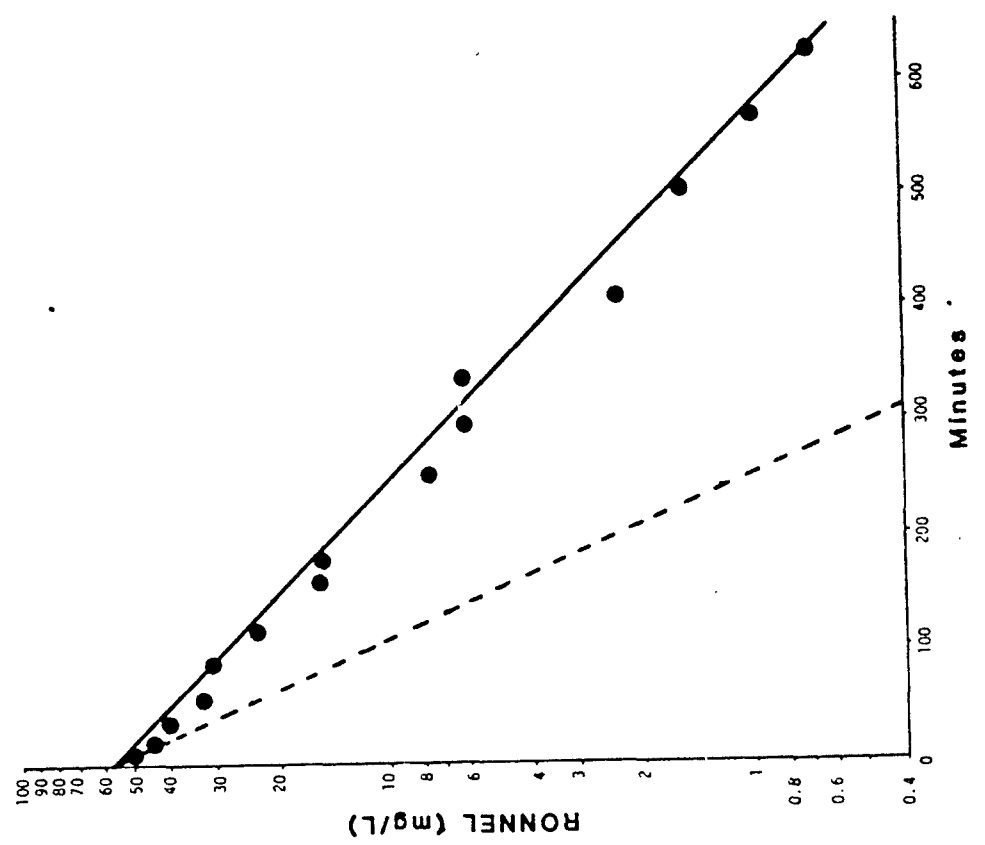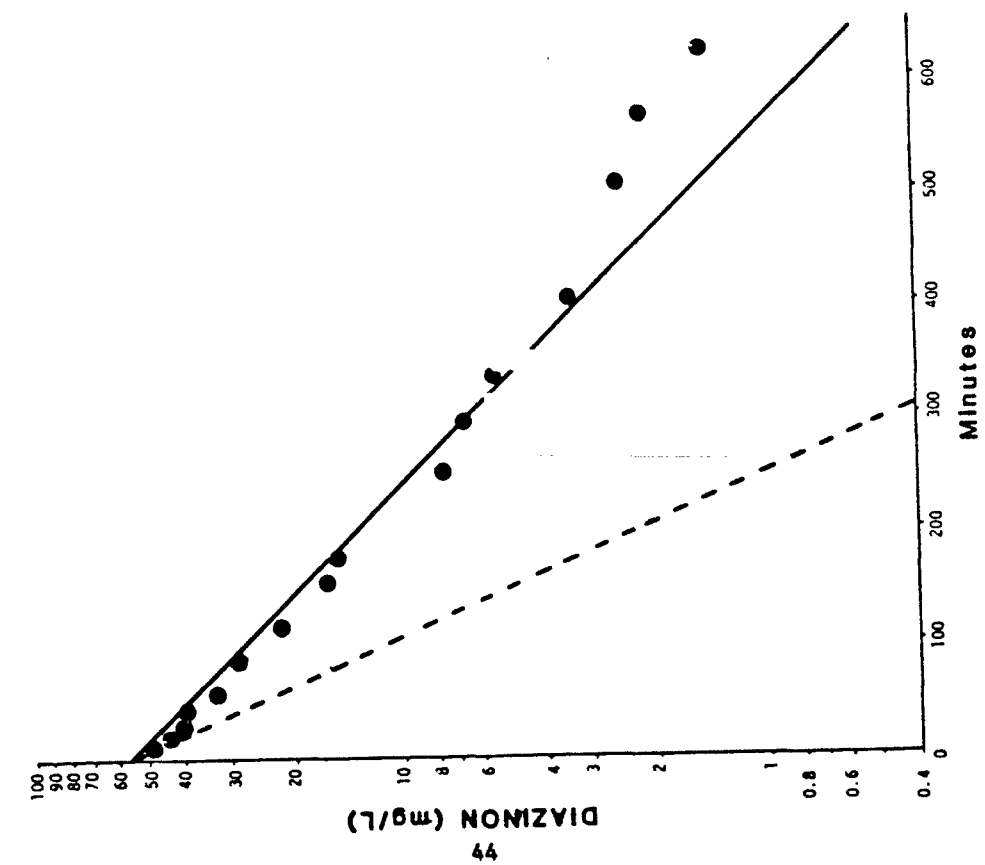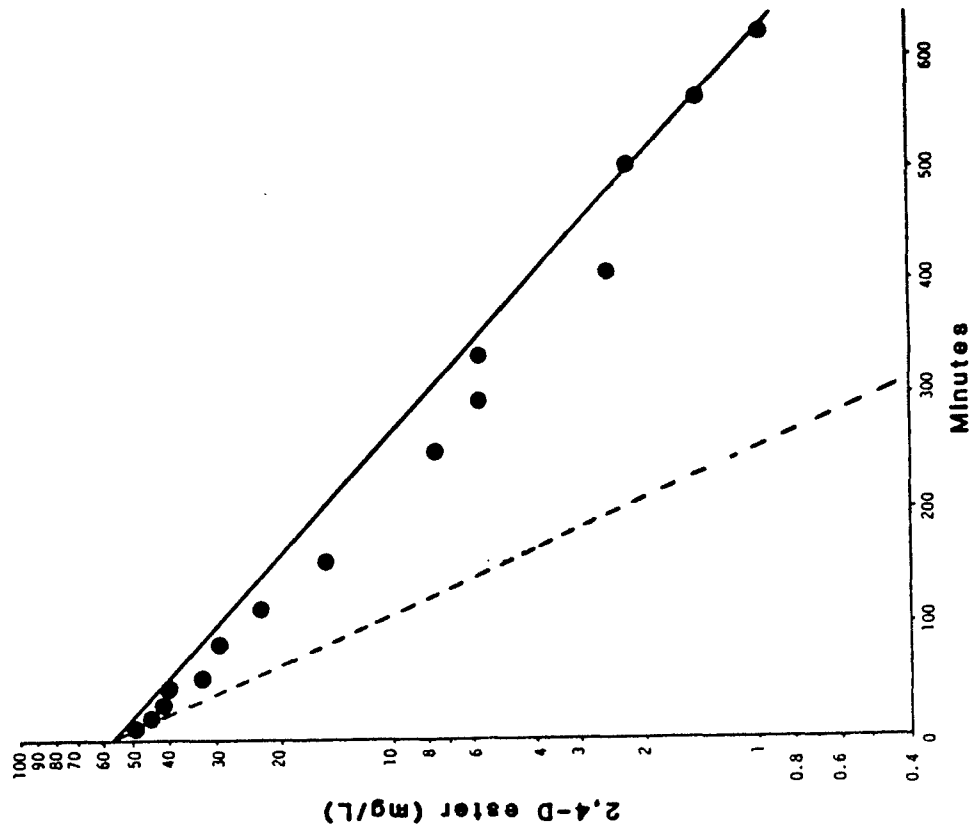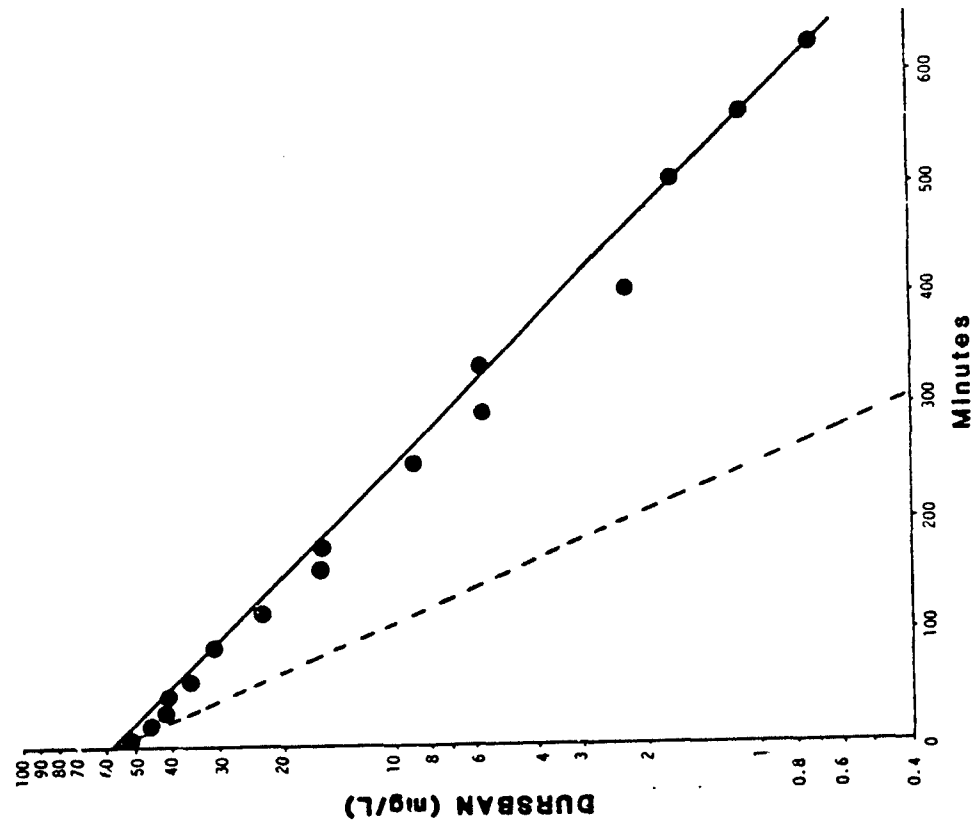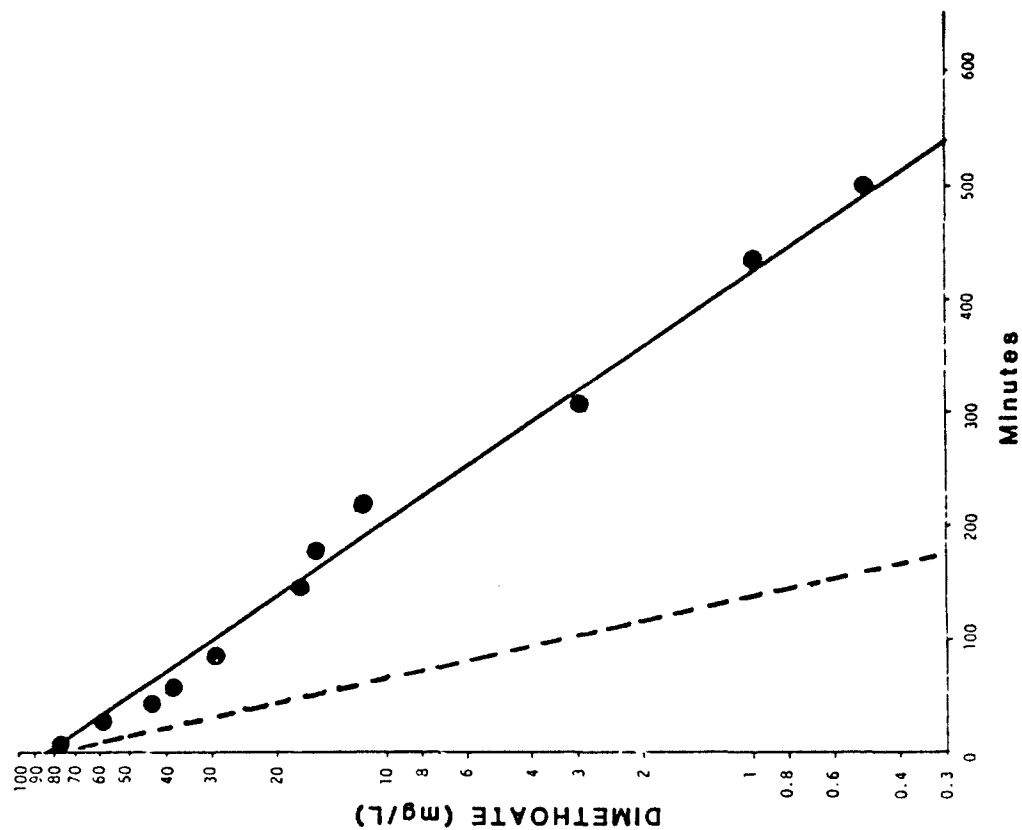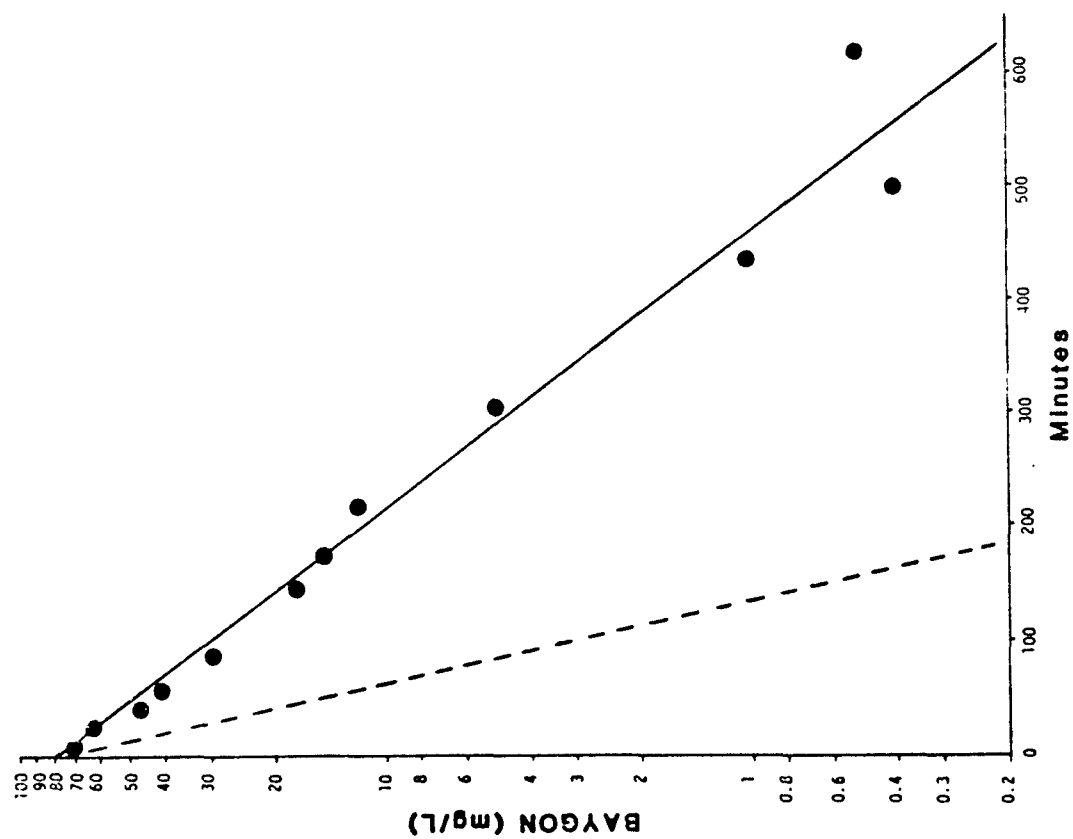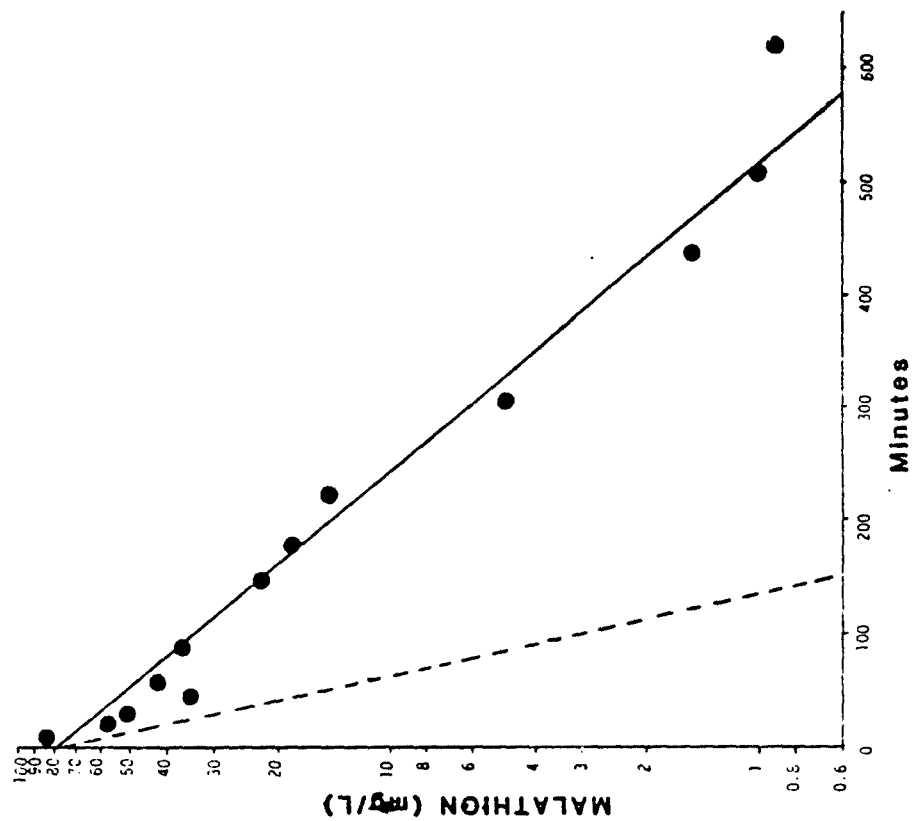

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Appendix A Continued

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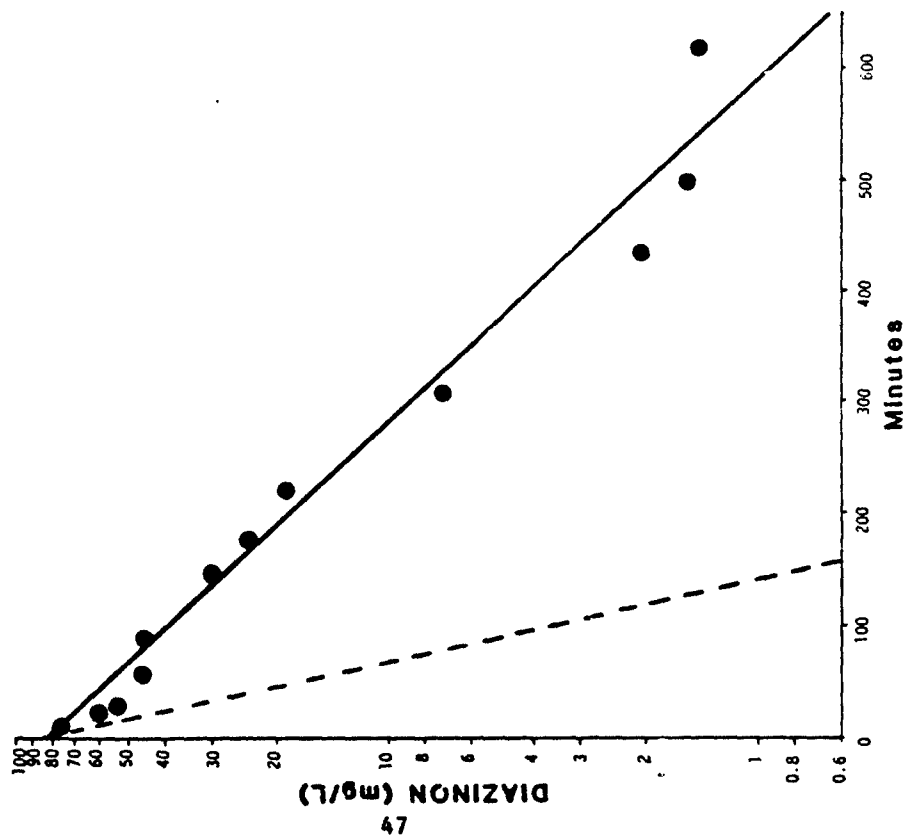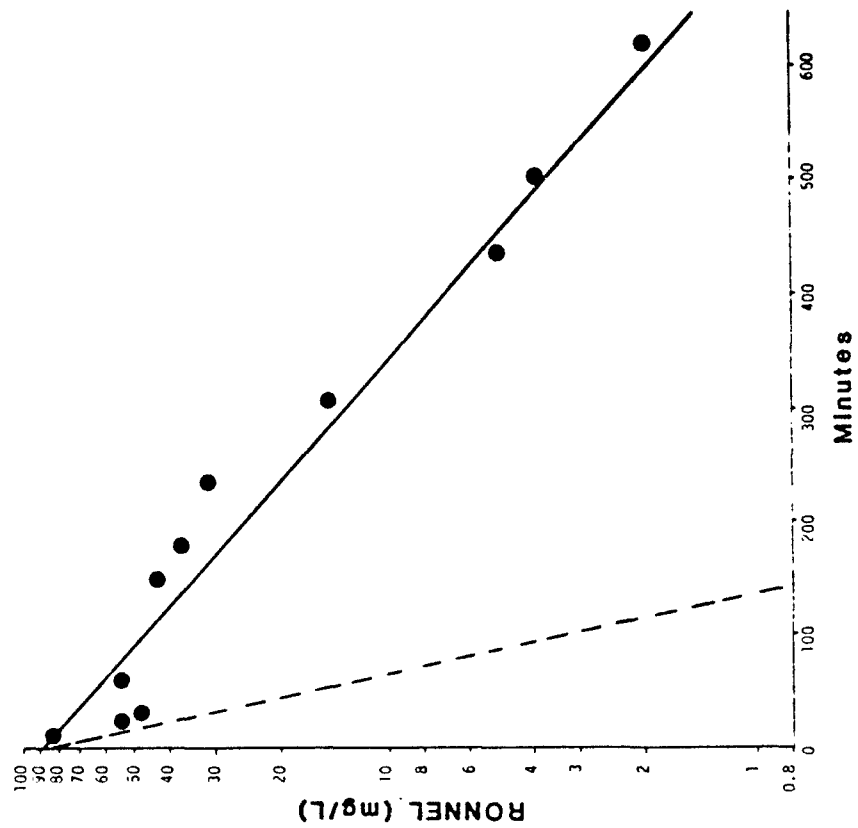Appendix A Continued

DURSBAN (mg/L)

RONNEL (mg/L)

Minutes

41
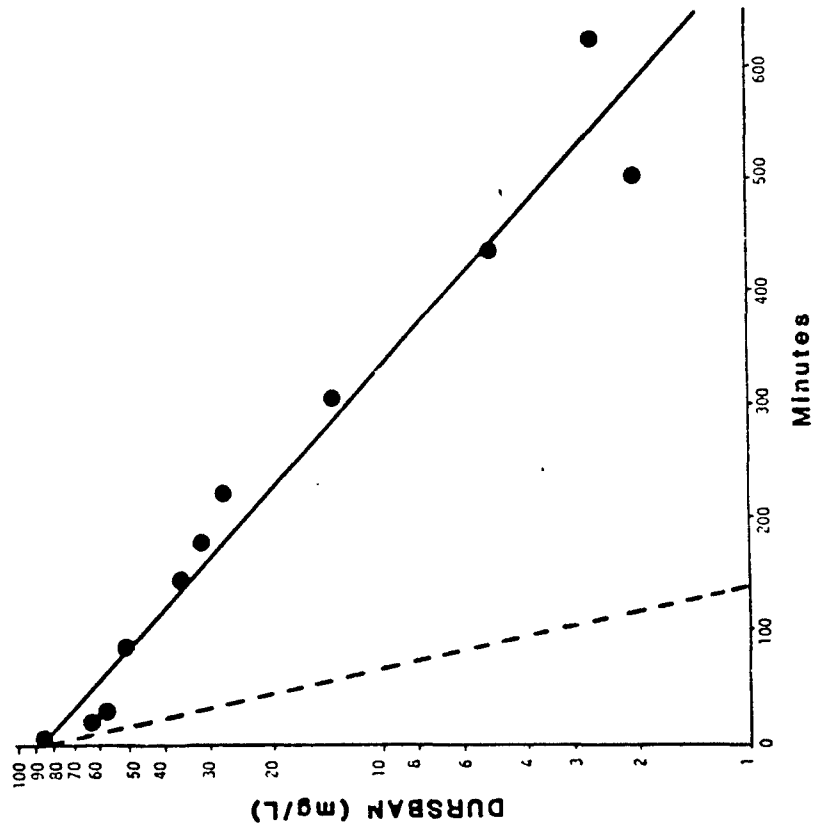
Appendix A Continued

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Appendix A Continued

43

Appendix A Continued

RONNEL (mg/L)

Minutes

DIAZINON (mg/L)

Minutes

44

Appendix A Continued

45

Appendix A Continued

46

Appendix A Continued

MALATHION (mg/L)   Minutes

DIAZINON (mg/L)   Minutes

47

Appendix A Continued

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Appendix A Continued

2,4-D ester (mg/L)

Minutes

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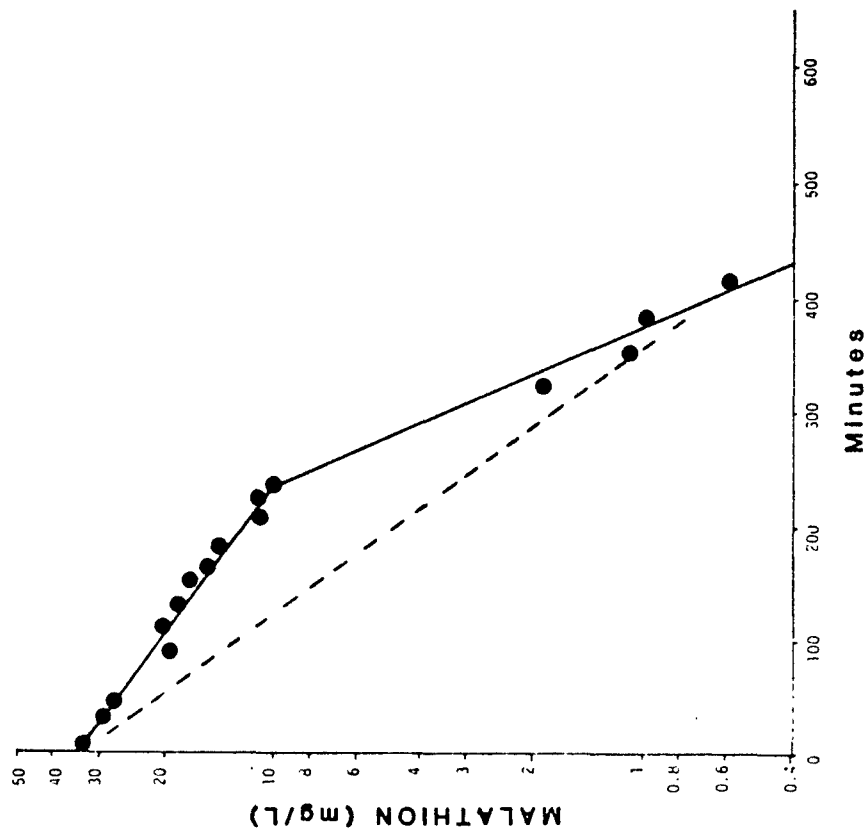## APPENDIX B

Concentration of pesticides in wastewater undergoing carbon filtration by the CARBOLATOR during the field test of July 1981 at Fort Eustis, VA. The dashed line indicates theoretical decline in concentration based on the complete removal of pesticide during a single pass at the given volume and flow rate.

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Appendix B Continued

BAYGON (mg/L)

Minutes

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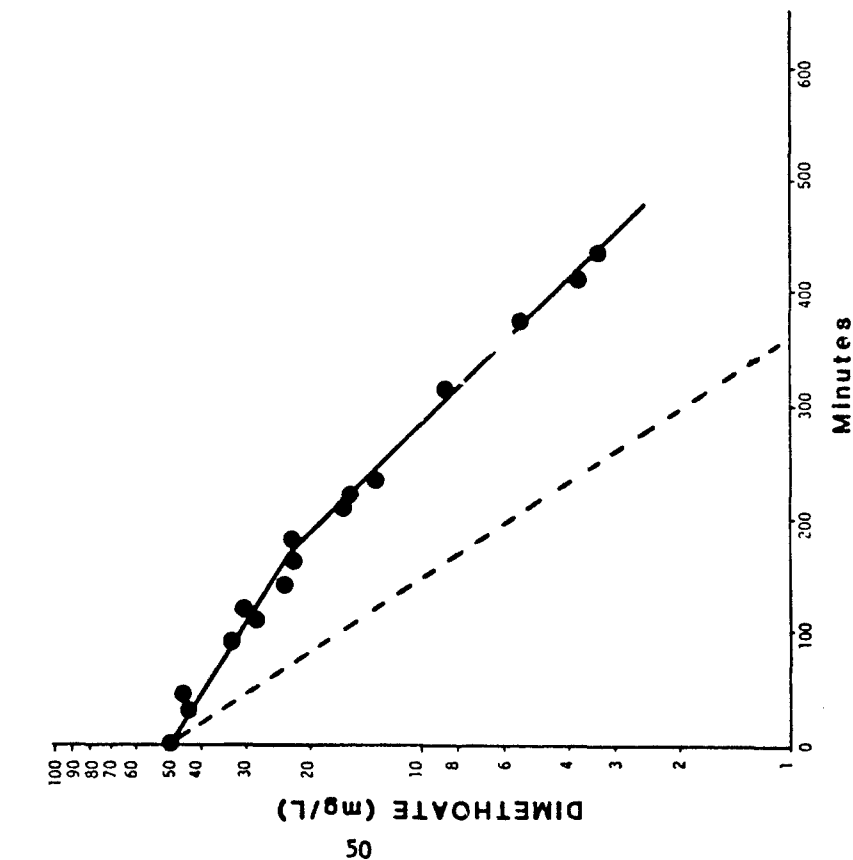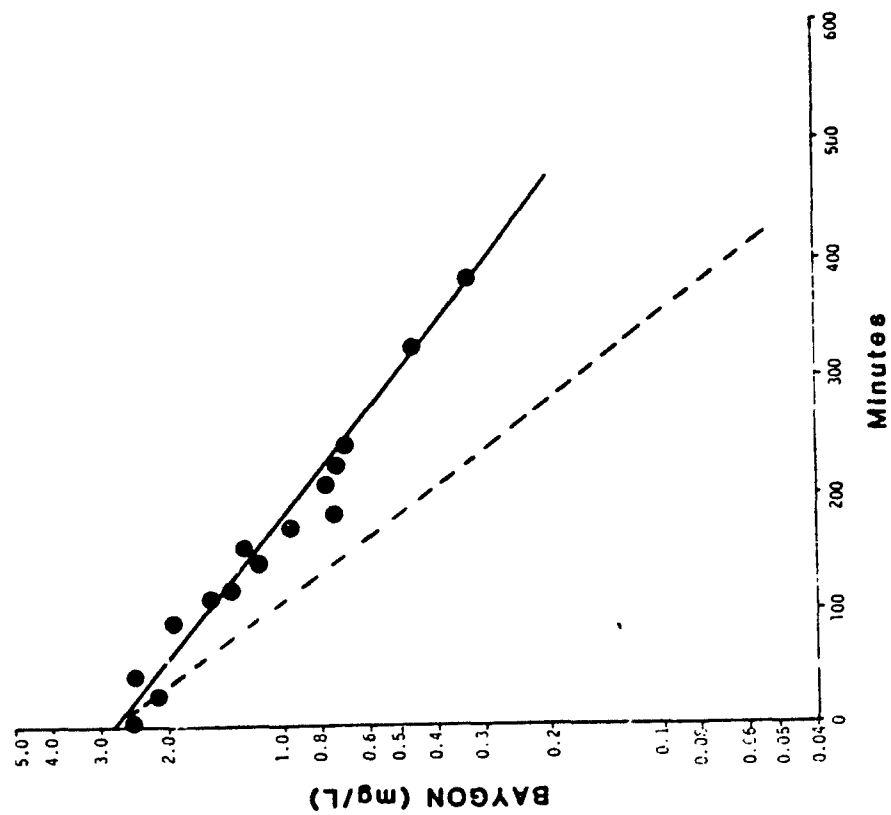## APPENDIX C

Concentration of pesticides in wastewater undergoing carbon filtration by the CARBOLATOR during the field test of September 1981 at Fort Eustis, VA. The dashed line indicates theoretical decline in concentration based on the complete removal of pesticide during a single pass at the given volume and flow rate.
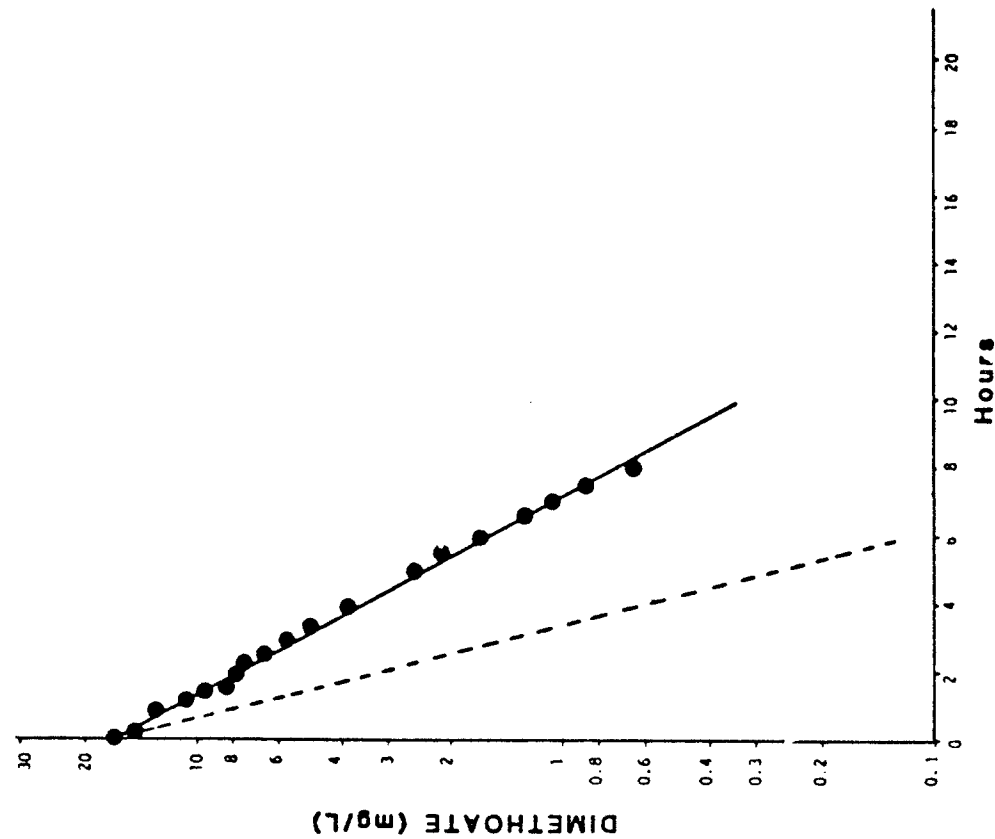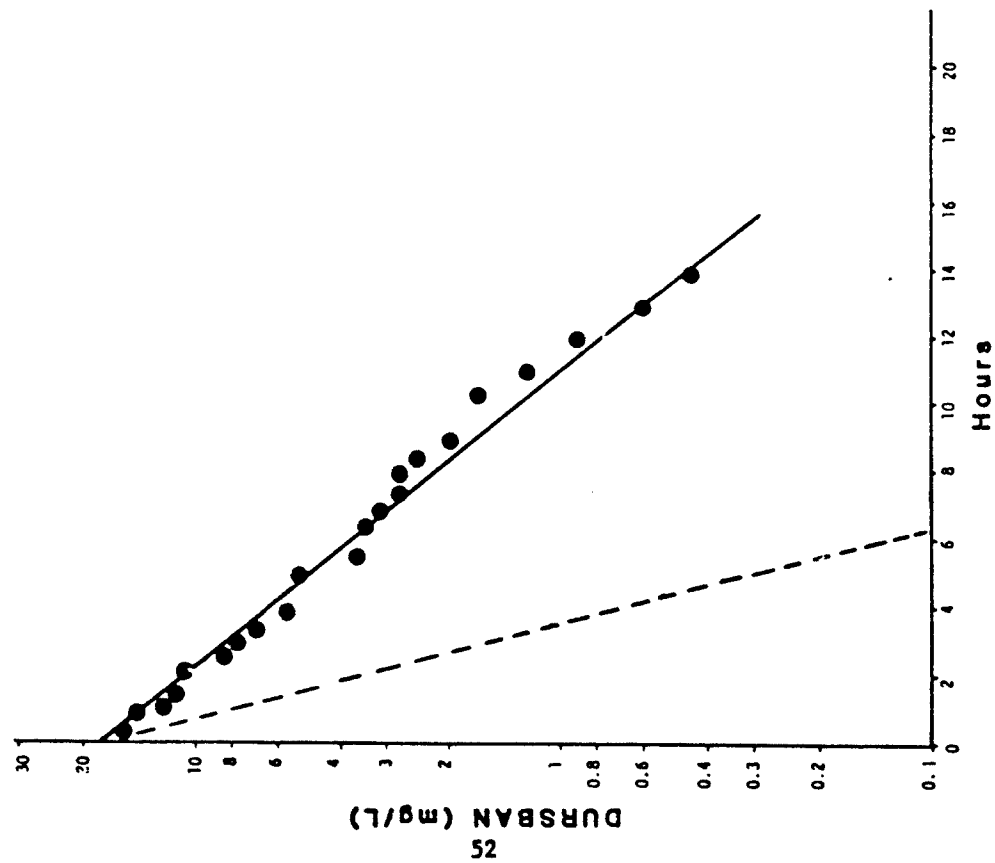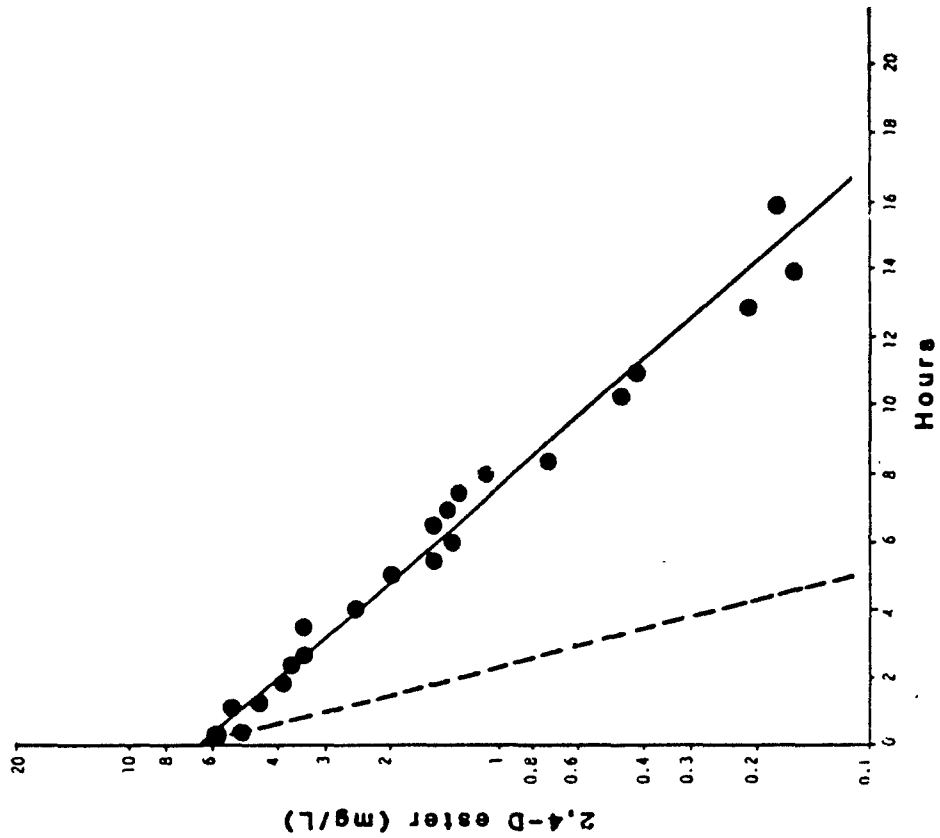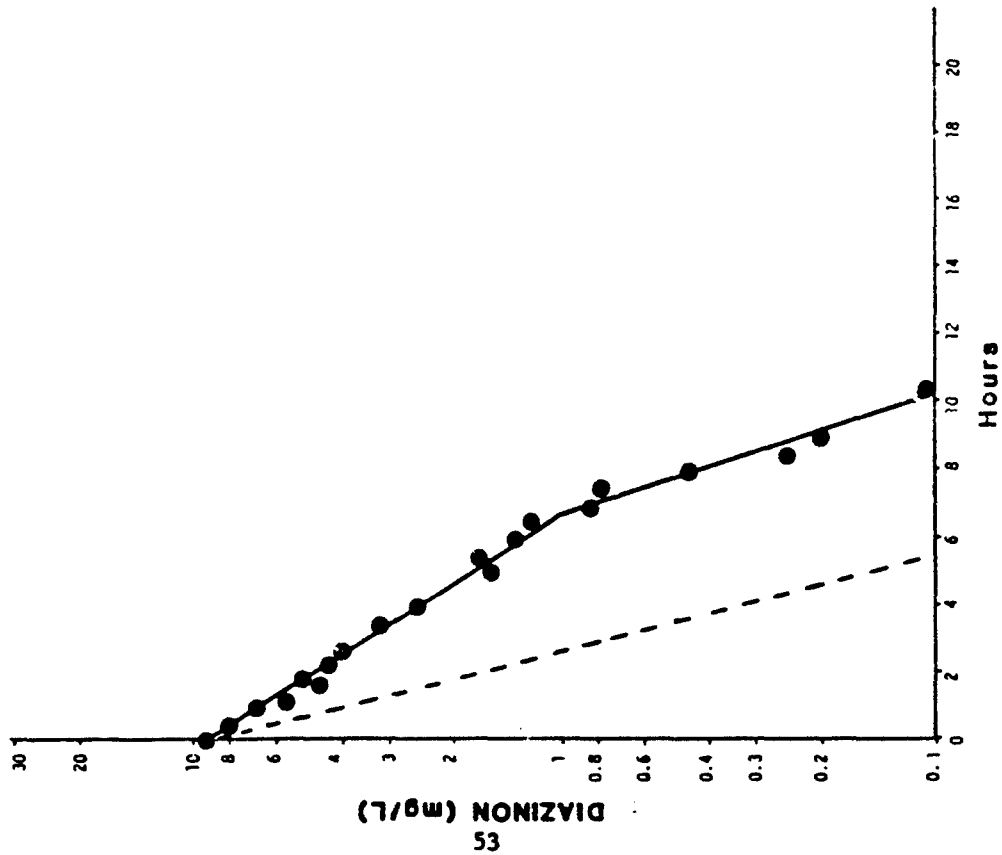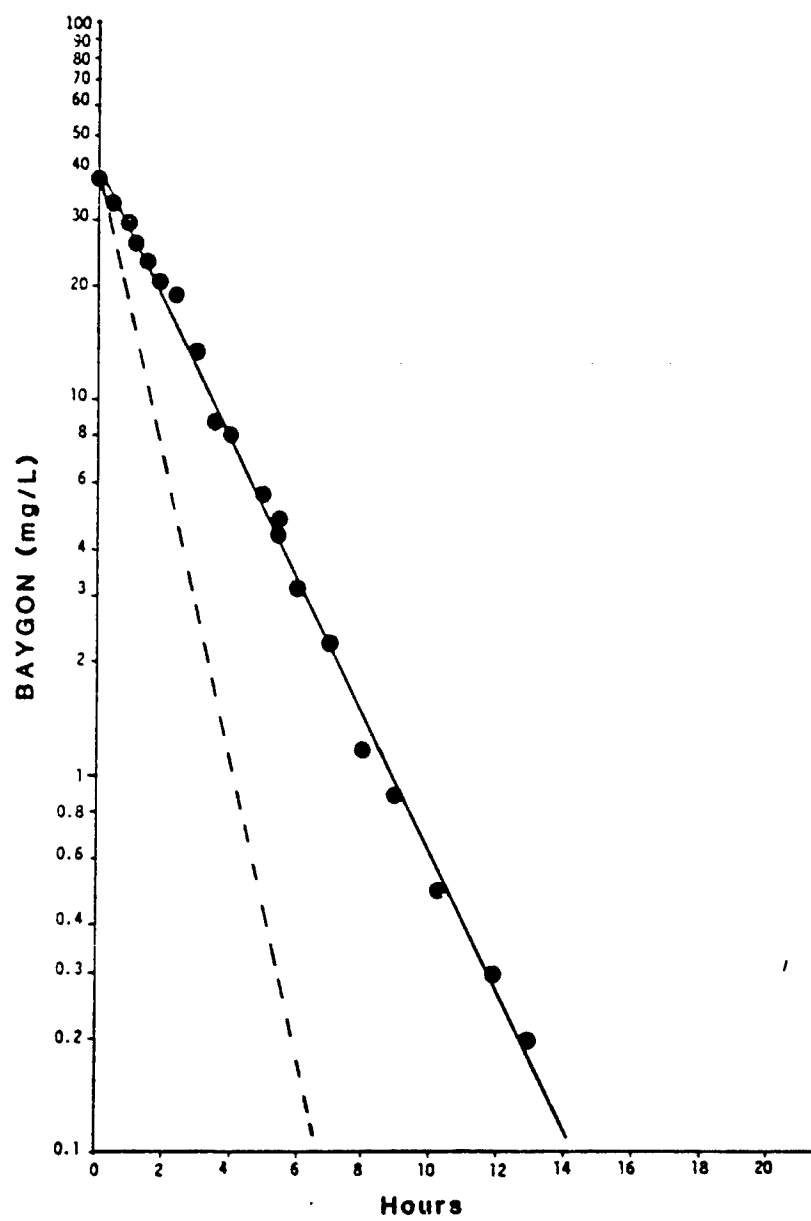

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Appendix C Continued

53

Appendix C Continued

APPENDIX D

Schematic drawing of the complete CARBOLATOR treatment train with components and their assemblage.

Flexible return line (tygon)

Cartridge filter

CARBOLATOR-35B

Pump, ¼HP, 30 GPM

500 gallon dish-bottom fiberglass tank

DESCRIPTIONS

1. 2", NPT* pipe outlet
2. 2", 90° elbow MPT
3. 2", MPT ball valve
4. 2", MPT union
5. 2" x NPT** reducer bushing
6. NPT** elbow
7. NPT** tee
8. NPT** reducer bushing
9. Ball valve for shut off and flow control
10. Union to disconnect line
11. Tee 1/2" or 3/4" NPT**
12. Flow control valve
13. Pressure gauge
14. Sample valve (optional)
15. Rotameter (optional)

* Nominal pipe thread
** Size will depend on pump inlet and outlet pipe thread

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